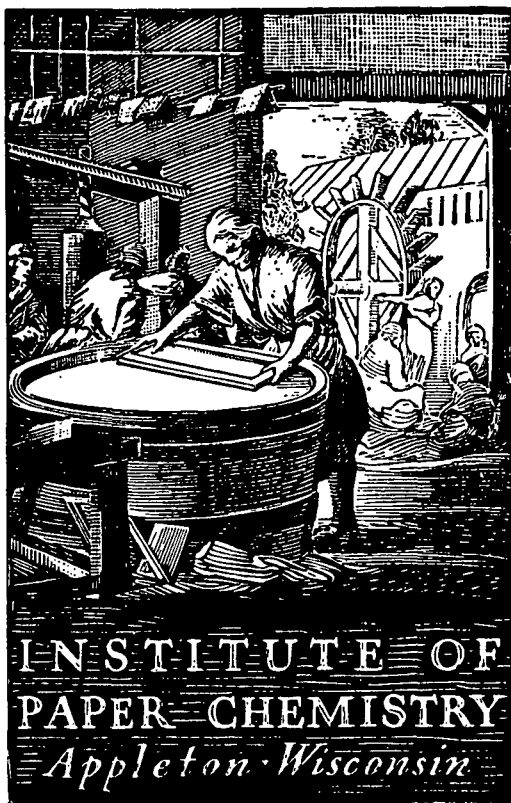


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**IMPROVED BONDING STRENGTH OF  
GROUNDWOOD FURNISHES:  
HARDWOOD AND SOFTWOOD PULPS  
JET-COOKED WITH CAUSTIC**

Project 2948

Report Two

A Progress Report

to

MEMBERS OF GROUP PROJECT 2948

August 4, 1972

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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HARDWOOD AND SOFTWOOD PULPS JET-COOKED WITH CAUSTIC

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Appleton Papers, Inc. - Locks Mill

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# THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

## IMPROVED BONDING STRENGTH OF GROUNDWOOD FURNISHES: HARDWOOD AND SOFTWOOD PULPS JET-COOKED WITH CAUSTIC

### SUMMARY

The bonding characteristics of hardwood pulps are improved by the alkali jet cooking treatments described in this report. This is shown by comparison of the physical properties of handsheets made from 80% of the treated pulp and 20% of softwood kraft pulp with properties of control handsheets containing varying proportions of the untreated groundwood and kraft pulps. The tensile strength of handsheets prepared from 80% treated aspen chemirefiner groundwood exceeded that of the control sheets made from 100% kraft. The tensile energy absorption of these 80% treated groundwood/20% kraft handsheets was as much as 104% of the control sheets containing 50% untreated groundwood and 50% kraft. Handsheets from 80% treated aspen stone groundwood and 20% kraft approached the all kraft control in tensile strength and the 50% untreated groundwood/50% kraft control in tensile energy absorption. The overall effect upon the properties of the 80/20 blends indicates that the treated pulp behaves more like a chemical pulp. The treatment increased tensile strength, tensile energy absorption, tensile stiffness, and apparent density. Tearing resistance and extensibility were unchanged.

Brightness of the groundwood pulp was decreased by the alkali treatment but this effect was prevented by including 2.5% hydrogen peroxide (based on pulp) in the treatment liquor. With larger concentrations of peroxide, the pulp was bleached during the treatment.

Yields of treated pulp range from 93 to 98% depending on the original pulp, the alkali concentration, and the temperature. Substantial amounts of

sodium hydroxide and peroxide remain in the slurry of treated pulp and are presumably available for recycling.

Treatment of either the hardwood chemirefiner or stone groundwood with 10% sodium hydroxide and 2-1/2% peroxide at 230°F. would permit replacement of 50% untreated groundwood/50% kraft furnishes with 80% treated groundwood/20% kraft furnishes with essentially the same tensile energy absorption, and improved tensile. Tear factor would be somewhat reduced. Assuming a 95% yield in the treatment process and a cost of chemical pulp twice the cost of the untreated groundwood, the saving in pulp cost per ton of furnish would be 19%. This saving must be weighed against treatment cost.

The properties of handsheets made from furnishes of treated softwood groundwoods and softwood kraft are also improved over control sheets containing the untreated groundwood but to a lesser degree than the aspen pulps. The best results were obtained at high temperature (290°F.), high caustic (15%), and high peroxide (7% with 10% NaOH). This indicates that softwood groundwood pulps require harsher processing conditions than hardwood pulp.

When deinked old newspaper pulp, which consisted of predominantly northern softwoods, was treated with alkali the tensile strength and tensile energy absorption both increased with increasing alkali content. However, when the same pulp was not deinked prior to alkali treatment, both of these properties decreased with increasing alkali content after attaining comparable levels for the other pulp treated with 5% caustic. Further work will be required to determine the reason for this difference.

## INTRODUCTION

This is Report Two for Project 2948 which was established at The Institute of Paper Chemistry to explore ways to improve the bonding strength of groundwood furnishes. In general, the physical strength of paper, as measured by the burst, tensile, and tear tests, is reduced in proportion to the groundwood in the furnish. This limits the amount of that pulp which may be used in place of the more expensive chemical pulps. The lower strength of groundwood furnishes is attributed to a lower capacity of these pulps to form strong fiber-to-fiber bonds and not, primarily, to a lower proportion of long fibers.

The strength of fiber-to-fiber bonds has been deduced to be a function of the degree to which short-range bonding forces, such as hydrogen bonding, are effective in promoting adhesion of one fiber to another (1). The fiber surfaces involved in bonding must approach one another very closely for such forces to become effective. The distance of separation should be no more than a few Angstrom units (1). Treatments which increase the ability of the fiber surface to conform, span voids, and enlarge the area of intimate molecular contact enhance the strength of the union between fibers. Beating and refining are operations commonly used to increase the plasticization and conformability of the chemical pulp surfaces. However, groundwood pulps usually do not respond to such treatments as much as is needed for greater use in mixed furnishes.

Chemical derivatization of the cellulose and hemicellulose components of groundwood pulps was considered to be one way to increase swelling and conformability of the fiber surfaces and thus improve bonding. This concept has been applied successfully to another kind of pulp which responded poorly to refining (2) and is the basis upon which this project was accepted and undertaken.

Consideration was given in Report One of this project, to the desirable qualities of a process having a high potential for commercial acceptance and their implications in regard to the kinds of chemical treatments which should be attempted. Among these qualities were the ideals of simplicity and adaptability to continuous operation. The reaction conditions for derivatization were restricted to aqueous systems on the basis of the inherent economic boundaries which also dictate high yields of treated pulp. Aqueous systems at pumpable groundwood consistencies would facilitate uniform blending of pulp and derivatizing reagents as well as having the capability of being drawn directly from pulp mill pipelines.

One ramification of this list of qualities is that most of the polysaccharide derivatives formed in aqueous systems require strongly alkaline media which also solubilizes part of the pulp. Furthermore, derivatives formed to enhance swelling and plasticization of the groundwood surface are also likely to become soluble if the reaction is carried beyond optimum levels. Thus, the balance between effectiveness and pulp yields weighs heavily in assessing the merit of treatments promoting fiber bonding. (Alternatively, some mechanism could be provided to retain or utilize the solubilized material.)

The need to retain the shape and form of a papermaking pulp, and to obtain high yields requires two-phase reactions between the pulp and the chemical reagents. This means the particle surface area governs the reactivity and that the fines component of the pulp is most susceptible to modification. In Report One, it was established that both the fine and coarser fractions of aspen stone groundwood could benefit from treatments to improve bonding and that it is reasonable to proceed with chemical treatments even though the major effect is likely to be upon the fine fraction.



The main thrust of the research program has been in the evaluation of the effects of treating groundwood with sodium hydroxide over a range of temperatures. This study provides information concerning the effect of alkali treatments such as would be needed for preparation of derivatives. However, the immediate concern is to determine whether or not treatment with caustic, in itself, will achieve the overall objective of the project.

The potential of treating groundwood with sodium hydroxide was indicated by the results of the work dealing with a pulp derivative described in Report One. The sodium hydroxide concentrations were high and several hours were involved in the treatment. Further work with the aspen stone groundwood led to processing of alkaline, 2% pulp suspensions in a continuous steam injection unit originally designed to jet-cook starch. For convenience, this treatment will be called the jet/alkali process.

A wide range of processing temperatures is available with this laboratory jet cooker and treatments can be carried out quickly and reproducibly as a semi-continuous operation. Exposure time of the pulp to temperatures above about 195°F. is limited by the dimensions and pumping rate of the cooker to about six seconds. Evaporative cooling, as the process stream is flashed to atmospheric pressure, cools the pulp suspension to this temperature.

It was shown in Report One that heating neutral streams of the aspen pulp, over a range of 150 to 310°F., had a small but uniform effect upon the tensile strength of mixed furnish handsheets. Substantial improvements in bonding strength (50 to 70% higher tensile) were obtained when the pulp was treated with 5% sodium hydroxide (on the weight of the pulp) and processed at 190, 230, and 270°F. The best results were obtained from the 230°F. processing temperatures.

Brightness values of the handsheets were depressed by the alkaline treatments. However, adding 5% hydrogen peroxide to suspensions containing 5 and 10% sodium hydroxide treated at 230°F. not only prevented discoloration but also bleached the pulp. The brightness levels of 80 and 50% groundwood handsheets (blended with kraft pulp) was increased 9 to 10 points over those of the untreated controls and 11 and 18 points over the alkali controls. The breaking length of the handsheets containing 80% of the pulp treated with 10% NaOH and 5% H<sub>2</sub>O<sub>2</sub>, exceeded that of the handsheets containing 50% of the untreated groundwood by more than 20% while the burst factors were about the same. These data established that it was technically feasible to consider simultaneous treatments to bleach and to improve bonding.

In 1955 Foote and Parsons (3) described a process for treating aspen groundwood with sodium hydroxide to obtain greatly improved bonding. Their process used sodium hydroxide concentrations like those used in Report One but they preferred to operate at 125 to 130°F. with retention periods of 2 hours. The treated pulp was thoroughly washed before bleaching in order to reduce bleach consumption.

Both the jet/alkali process evolved in Report One and that of Foote and Parsons have several common features. However, the unusually short processing time with the jet cooker, the inherent capability of continuous operation, and the existence of jet cooking units already being used to heat pulp continuously into the headbox (4) and into bleaching units (5) make further evaluation of jet-cooked alkaline pulps desirable.

The work described here in Report Two, is directed toward determining: pulp yields, the amount of caustic and peroxide remaining in the process liquor,

the responsiveness of other kinds of groundwood, and the effect of processing temperature upon peroxide bleaching. In addition, a direct comparison is made between the performance of cooked and raw pulp treated with sodium hydroxide.

The experimental procedures for treating and evaluating the pulps are given in detail in the Appendix. Briefly, the pulps were jet-cooked at 2% consistency with 0, 5, 10, or 15% NaOH at 230°F. and with 10% NaOH and 1, 3, 5, or 7% H<sub>2</sub>O<sub>2</sub> at the same temperature. Temperatures of 230, 260, and 290°F. are used with 10% NaOH and 3% H<sub>2</sub>O<sub>2</sub>. The pulps used are an aspen stone groundwood (decker sample from the mill supplying the pulp used in Report One), an aspen chemirefiner pulp, a commercial fluff-dried softwood groundwood pulp, old newspapers, and deinked newspapers. The bonding of the virgin pulps was assessed by testing the strength of handsheets made from mixed furnishes containing 80% groundwood and 20% bleached softwood kraft. Since the newsprint pulps already contained a similar proportion of chemical pulp, the bleached kraft was not added to these furnishes. Investigation of the effect of temperature upon bleaching was omitted from this series of handsheets in order to be able to make at least a preliminary study of the effect of heat and alkali on both forms of the reclaimed newsprint. All of the handsheets were formed at pH 5 (H<sub>2</sub>SO<sub>4</sub>).

The physical properties of the handsheets prepared from 80% of treated groundwood are compared to those of control sheets made from 100% kraft, 50% untreated groundwood and 50% kraft, and 80% untreated groundwood and 20% kraft. This provides a means of estimating the amount of treated groundwood which can be substituted for the more expensive chemical pulp without impairing the physical properties as well as providing a frame of reference for the paper-making method.

## RESULTS AND DISCUSSION

### SODIUM HYDROXIDE TREATMENT WITH AND WITHOUT JET COOKING

In the preceding report, the tensile strength of mixed furnish ground-wood handsheets was increased by high concentrations of sodium hydroxide (e.g., 30%) by allowing the pulp to stand at room temperature for several hours. Jet-cooking in itself improved the strength to some extent, and jet cooking with lower concentrations of sodium hydroxide (up to 10%) produced remarkable improvements in tensile strength. The implication was that the heat and caustic together were producing the desired strength elevation. However, there was no direct evidence that the jet cooker in itself was actually producing an effect with the alkaline system. Thus, it was not known with certainty that the jet cooker was needed. To answer this question the following experiment was carried out.

A 2% suspension of aspen stone groundwood was prepared with 10% sodium hydroxide added on the dry weight of the pulp. Part of the suspension was jet-cooked at 230°F. and the other part was allowed to stand (18°C.) until after the heated pulp had been cooled and neutralized. The raw pulp was then neutralized after an exposure to the alkali of about 40 minutes. Both pulps were blended with bleached softwood kraft pulp (80 parts groundwood/20 parts kraft) and made into handsheets. A third set of handsheets was made up from groundwood which had received no treatment other than having been redispersed for 300 counts in a British disintegrator. All three sets were formed at pH 5; adjusted to that value with dilute  $H_2SO_4$ . The results of the testing program are given in Table I.

Inspection of the data in Table I reveals that jet cooking with 10% NaOH produces by far the strongest handsheets. The caustic treatment by itself is not

TABLE I

EFFECT OF CAUSTIC TREATMENT WITH AND WITHOUT JET COOKING UPON THE  
PROPERTIES OF HANDSHEETS FROM FURNISHES OF 80% GROUNDWOOD  
AND 20% KRAFT

Measurement	Control No Caustic	Raw Slurry <sup>a</sup> 10% NaOH	Cooked Slurry <sup>b</sup> 10% NaOH
Ref. No.	131	130	129
Pulp yield, %	98.7	97.6	95.0
Pulp brightness, %	63.1	58.8	48.9
Blended brightness, %	64.8	61.8	52.7
Opacity, %	93.9	93.4	92.1
Apparent density, g./cc.	0.385	0.428	0.503
Bendtsen porosity, ml./min.	401	218	57
Tear factor, m. <sup>2</sup>	60.1	68.4	65.9
Breaking length, km.	3.05	2.40	4.33
Tensile energy absorption, g.cm./cm. <sup>2</sup>	29.0	18.2	40.9
Stretch, %	2.1	1.7	2.1
Tensile stiffness, kg./cm.	244	205	332
Basis weight, g./m. <sup>2</sup>	63.6	62.9	62.4

---

<sup>a</sup> 64°F.

<sup>b</sup> 230°F.

sufficient to bring about the desired changes, within 40 minutes, and appears to have a generally harmful effect upon the handsheet properties. Consequently, both the jet cooker and the sodium hydroxide are needed to produce improved bonding of groundwood mixed furnishes, at least within the processing times being considered.

#### HARDWOOD AND SOFTWOOD PULP TREATMENTS

Data for the 80% groundwood handsheets discussed in this section are given in Tables II to IV. The pulps were blended with 20% bleached softwood kraft for testing the results of the treatments. A description of the pulps and the operating procedures is given in the Appendix of this report.

#### Brightness

The pulp browning brought about by the sodium hydroxide treatments obviously must be dealt with in some manner so that the greater strength of the pulp may be utilized. Foote and Parsons (3) state that the pulp brightness is easily reclaimed by conventional bleaching if the pulp is washed beforehand. Their data show a loss of 14.4 points brightness for aspen stone groundwood treated for 2 hours in 10% NaOH at 120°F. This loss is almost identical to the 14.2 points lower brightness shown in Table I for the pulp jet cooked at 230°F. with 10% NaOH.

In Report One, it was shown that browning was avoided and bleaching occurred when 5% hydrogen peroxide was added to the raw suspension before jet cooking at 230°F. The advantages of combining two operations require further investigation into the degree of bleaching which can be obtained and the amount of reagent required. Further, both the evidence given in Report One and the

TABLE II  
 ASPEN STONE GROUNDWOOD: EFFECT OF TREATMENTS UPON THE PROPERTIES OF HANDSHEETS FROM FURNISHES  
 OF 80% GROUNDWOOD AND 20% KRAFT

Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature	Groundwood Brightness, %	Paper Brightness, %	Opacity, %	Density, g./cc.	Tear Factor, m. <sup>2</sup>	Breaking Length, km.	TEA, g.-cm./cm. <sup>2</sup>	Stretch, %	Tensile Stiffness, kg./cm.	Bendtsen Air Permeation Rate, ml./min.	Basis Weight, g./m. <sup>2</sup>
85	0	0	230	--	64.5	93.5	0.375	64.2	2.52	19.5	1.7	212	421	62.6
86	5	0	230	--	57.8	92.4	0.448	67.5	3.68	28.8	1.8	306	124	60.9
87	10	0	230	--	52.4	91.3	0.510	63.4	4.91	42.2	1.9	405	47	64.2
89	10	1	230	--	58.3	88.3	0.516	65.2	5.10	54.2	2.3	387	41	63.5
90	10	3	230	--	68.3	86.6	0.514	63.6	4.80	42.9	2.0	377	42	63.2
91	10	3	260	64.9	67.1	86.8	0.507	64.4	4.70	39.4	1.9	373	42	62.4
92	10	3	290	68.0	66.3	87.3	0.509	64.2	4.75	47.5	2.2	364	43	63.1
95	10	5	230	69.4	71.6	86.4	0.505	65.7	4.67	41.1	2.0	355	55	62.6
96	10	7	230	73.3	74.8	85.8	0.502	67.5	4.89	48.1	2.1	370	52	63.3
88	15	0	230	--	51.0	91.5	0.506	64.5	4.91	42.1	1.9	395	40	63.7
93	15	3	246	60.8	64.4	85.8	0.524	65.2	5.00	44.9	2.0	390	35	62.4
94	15	3	290	57.8	61.5	87.1	0.518	67.3	5.18	55.9	2.3	395	38	64.2
<u>Controls</u>														
83	All kraft			--	86.2	73.4	0.530	144.8	5.45	94.5	3.9	359	198	63.1
83	50/50 Untreated groundwood/kraft			--	67.9	87.8	0.426	120.4	3.33	45.1	2.9	248	334	61.3
83	80/20 Untreated groundwood/kraft			--	64.8	93.2	0.386	61.8	2.42	23.2	2.0	200	382	63.3

TABLE III  
ASPEN CHEMIFIBER GROUNDWOOD: EFFECT OF TREATMENTS UPON THE PROPERTIES OF HANDSHEETS FROM  
FURNISHES OF 80% GROUNDWOOD AND 20% KRAFT

Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature, °F.	Groundwood Brightness, %	Paper Brightness, %	Opacity, %	Density, g./cc.	Tear Factor, m. <sup>2</sup>	Breaking Length, km.	TEA, g.cm./cm. <sup>2</sup>	Stretch, %	Tensile Stiffness, kg./cm.	Bendtsen Air Permeation Rate, ml./min.	Basis Weight, g./m. <sup>2</sup>
97	0	0	230	48.9	53.8	86.4	0.401	81.6	4.76	44.9	2.2	316	104	62.1
99	5	0	230	42.7	47.6	85.2	0.477	80.0	5.78	57.7	2.2	405	35	62.9
110	10	0	230	39.9	45.3	83.4	0.504	72.0	5.96	59.2	2.2	417	28	62.9
101	10	1	230	43.9	49.5	81.2	0.498	77.0	6.10	66.0	2.4	424	27	63.8
102	10	3	230	52.3	57.4	79.0	0.497	73.3	6.12	64.3	2.4	413	26	62.6
105	10	3	260	52.0	56.6	79.6	0.498	74.4	5.25	43.3	1.9	389	24	61.7
106	10	3	290	48.7	53.9	81.3	0.476	77.2	5.34	49.9	2.1	387	34	62.4
98	15	0	230	38.6	44.3	82.9	0.506	74.1	6.31	66.6	2.4	420	23	61.7
103	10	5	230	56.9	61.8	77.9	0.493	74.7	5.40	48.3	2.0	391	16	62.1
104	10	7	230	60.4	64.6	77.6	0.500	78.4	5.49	45.1	1.9	396	24	61.5
<u>Controls</u>														
84	50/50 Untreated groundwood/kraft			--	60.0	81.7	0.443	114.3	4.81	64.1	3.0	323	140	61.6
84	80/20 Untreated groundwood/kraft			--	54.3	85.4	0.425	78.0	4.49	42.9	2.1	324	85	63.3



TABLE IV  
SOFTWOOD MARKET GROUNDWOOD: EFFECT OF TREATMENTS UPON THE PROPERTIES OF HANDSHEETS FROM  
FURNISHES OF 80% GROUNDWOOD AND 20% KRAFT

Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature, °F.	Pulp Brightness, %	Paper Brightness, %	Opacity, %	Density, g./cc.	Tear Factor, m. <sup>2</sup>	Breaking Length, km.	TEA, g.cm./cm. <sup>2</sup>	Stretch, %	Tensile Stiffness, kg./cm.	Bendtsen Air Permeation Rate, ml./min.	Basis Weight, g./m. <sup>2</sup>
108	0	0	230	53.8	56.6	92.2	0.353	74.7	2.92	22.9	1.8	224	731	62.4
109	5	0	230	47.4	50.4	93.8	0.399	78.2	3.43	25.7	1.7	274	354	63.9
110	10	0	230	44.9	48.1	93.7	0.404	75.9	3.46	26.4	1.7	285	363	63.0
112	10	1	230	45.4	48.4	92.8	0.407	71.7	3.41	23.3	1.7	285	328	62.2
113	10	3	230	47.9	50.3	92.2	0.412	74.3	3.43	24.7	1.7	286	319	63.9
116	10	3	260	47.4	50.6	91.9	0.415	76.7	3.66	27.6	1.8	294	288	62.3
117	10	3	290	47.2	49.9	91.8	0.433	74.2	3.93	30.6	1.8	312	186	63.2
114	10	5	230	50.0	52.5	91.7	0.416	76.6	3.60	25.7	1.7	303	284	64.1
115	10	7	230	50.8	53.5	90.0	0.423	76.8	3.79	28.9	1.8	312	248	63.4
111	15	0	230	43.4	45.5	94.2	0.408	72.7	3.53	28.5	1.8	285	352	64.1
<u>Controls</u>														
84	50/50	Untreated groundwood/kraft	--	--	61.5	85.6	0.379	114.1	3.32	39.0	2.6	243	793	60.3
84	80/20	Untreated groundwood/kraft	--	--	57.8	90.6	0.334	65.6	1.97	13.9	1.6	181	1718	63.1

results of Foote and Parsons indicate that bleaching reduces the strength gain due to the alkali. This factor, however, will be discussed in a later section.

In Fig. 1 to 3, the trends with increasing amounts of caustic and peroxide and rising processing temperatures are similar for the stone and refiner hardwood pulps and the softwood pulp. Brightness is reduced by increasing amounts of sodium hydroxide and raised by increasing amounts of peroxide with 10% NaOH at 230°F. Elevating the processing temperature from 230 to 260° and then to 290°F. with 10% NaOH and 3% H<sub>2</sub>O<sub>2</sub> reduces the brightness of the mixed furnish by 2 to 4 points over the entire temperature range for the two hardwood pulps (Fig. 1 and 2) and has almost no effect upon the softwood pulp (Fig. 3). The significance of the trend with the softwood pulp is obscured by anomalies in the behavior of this pulp which will become evident as the discussion proceeds. It does appear that more bleaching reagent is required for the aspen pulps as the processing temperature is raised.

The responses of the two aspen pulps to alkali and peroxide are comparable when the differences in the initial brightness levels are taken into account. The curves plotted in Fig. 1 and 2 indicate that the original brightness of the mixed furnish may be restored by about 2.5% peroxide with 10% NaOH at 230°F. Over the range of 0 to 7% peroxide the stone pulp mixed furnishes gain 18.8 points and those of the chemirefiner pulp 19.3. The highest pulp brightness obtained is 73.3% for the aspen stone groundwood treated with 7% peroxide and 10% NaOH at 230°F. (a gain of 24.4 points over the alkali darkened control in Table I). This compares with the brightness values Foote and Parsons (3) report for caustic-extracted aspen groundwood bleached with 2.5% sodium peroxide and with 10% chlorine. However, their initial brightness levels were higher since they were bleaching pulps extracted with less than 5% NaOH.

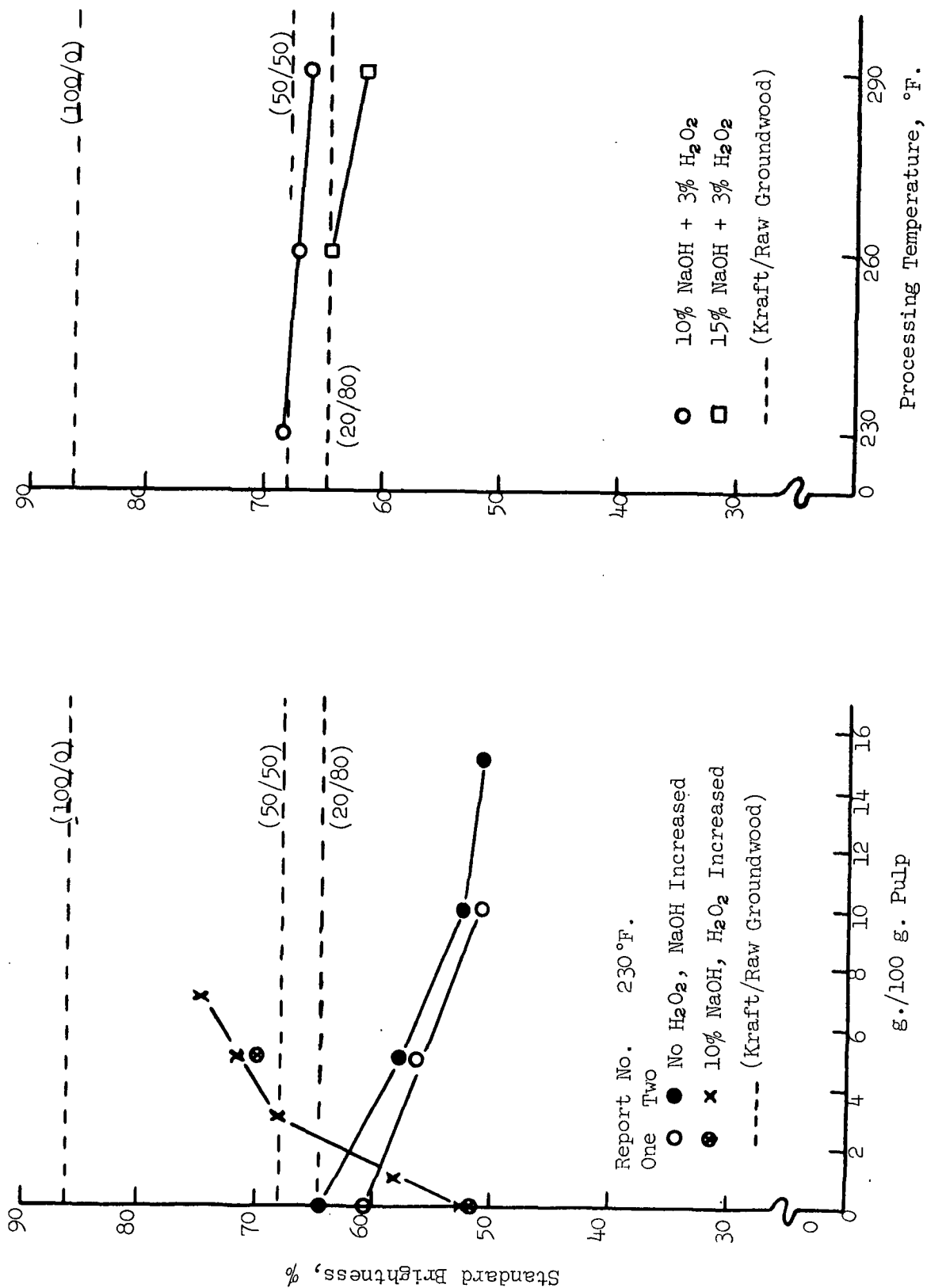


Figure 1. 80% Aspen Stone Pulp: Standard Brightness vs. Treatment

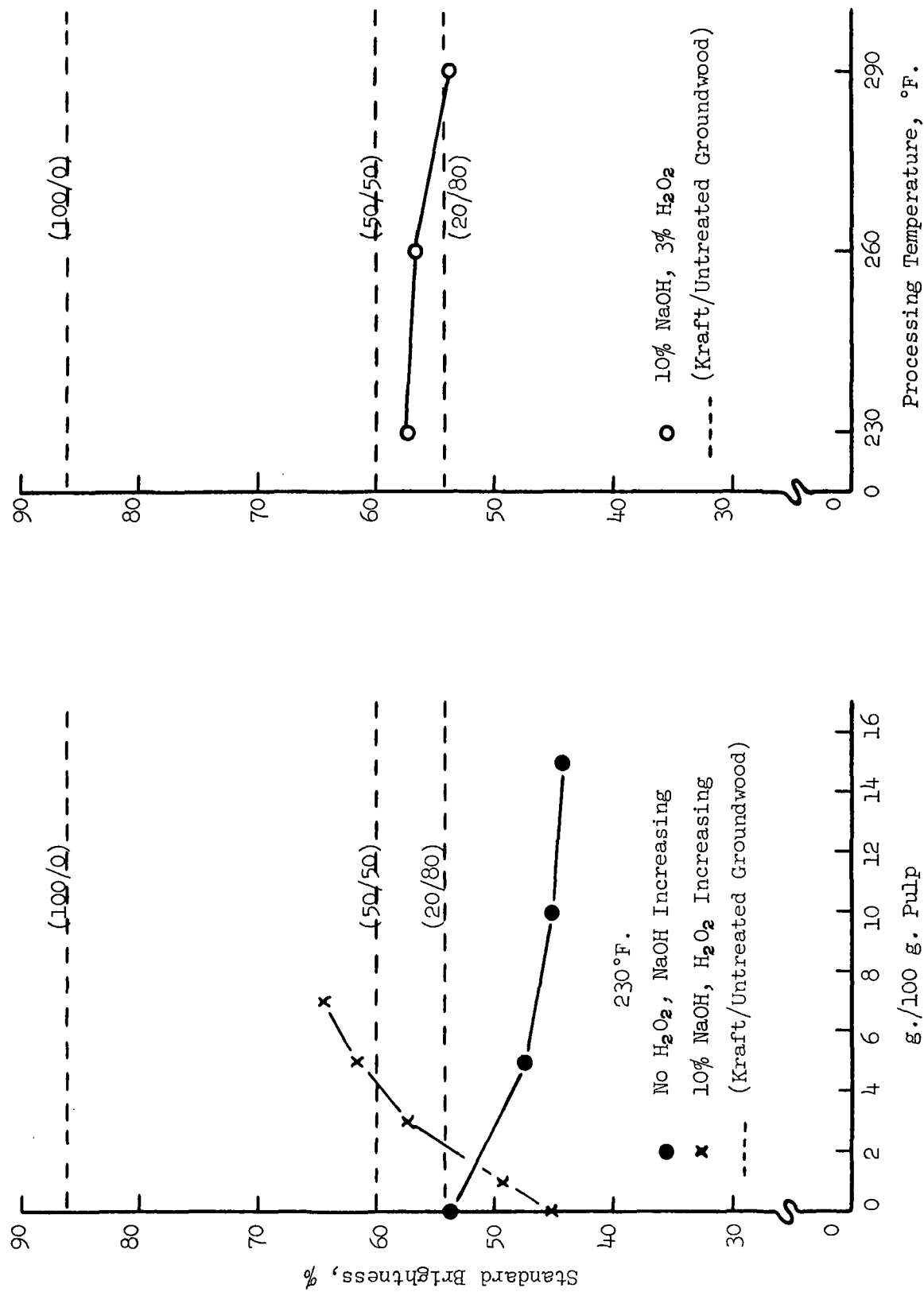


Figure 2. 80% Aspen Chemirefiner Pulp: Standard Brightness vs. Treatment

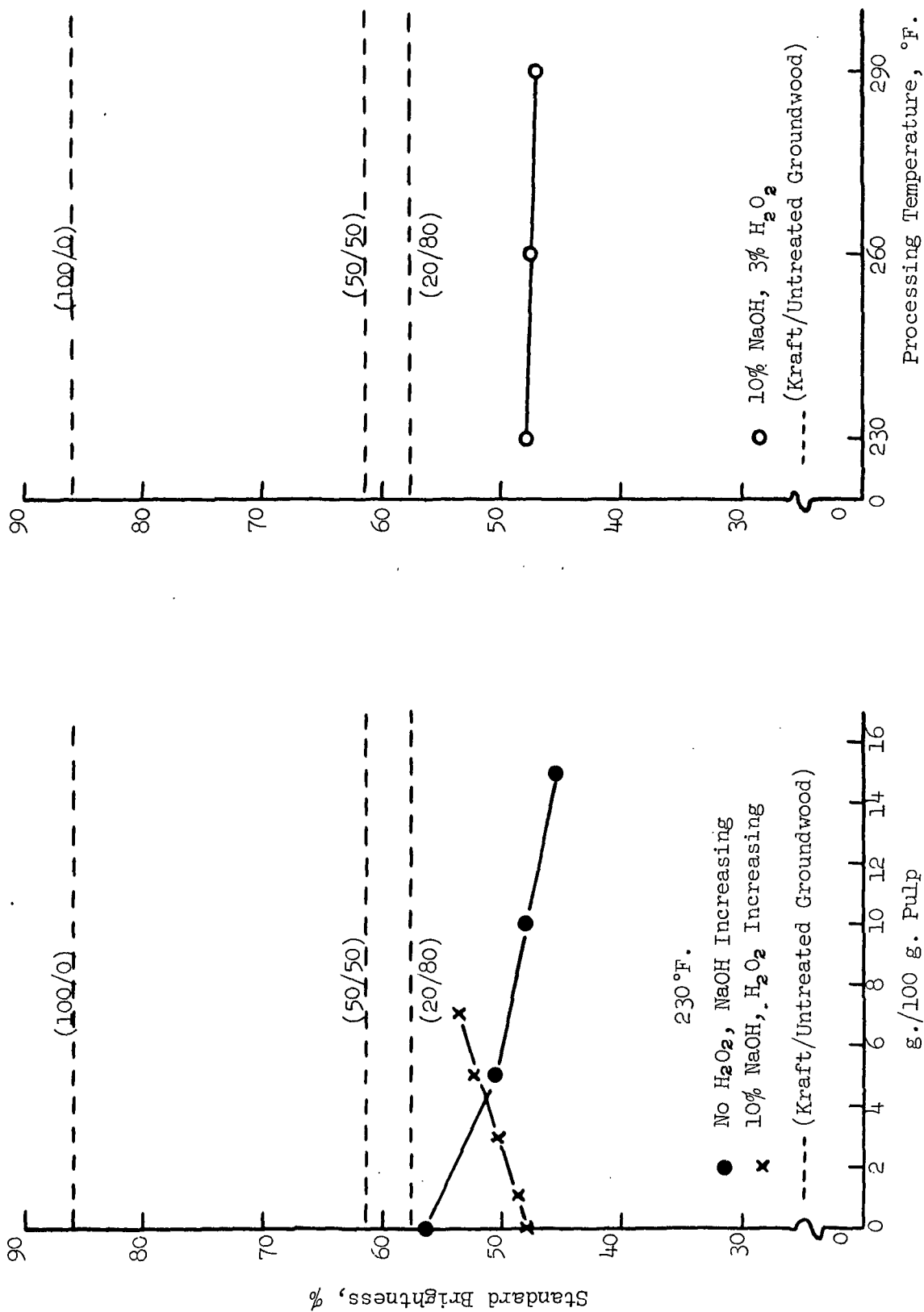


Figure 3. Fluff-Dried Softwood Pulp: Standard Brightness vs. Treatment

The fluff-dried commercial softwood groundwood, Fig. 3, is not effectively bleached by peroxide under the conditions used in these experiments. The highest addition level, 7%, does not even overcome the browning effect of the 10% NaOH. Yet in the case of the softwood pulps derived from the deinked newspaper, to be discussed later on, about 2.5% peroxide overcomes the darkening effect of 10% caustic. Thus, the data from this particular pulp probably is not typical of softwood pulps in general.

It is known that peroxide oxidizable dissolved solids in bleaching systems will reduce the concentration of peroxide available to bleach the pulp (6). Thus, it could be expected that combining bleaching with jet-cooking alkali groundwoods might increase the peroxide demand. However, it was not expected that major portions of the peroxide would be left over after the treatment. In Fig. 4, the amount of peroxide remaining in the aqueous phase after jet cooking, cooling, and neutralizing the caustic is plotted as percent of the amount added, versus the amount added on the weight of the pulp. The percent unreacted increases from 20 to 60% for the aspen stone groundwood as the hydrogen peroxide added is raised from 1 to 7% of the dry pulp weight. The data for the aspen chemirefiner pulp are slightly more scattered but cover about the same range. This means further bleaching should be possible by recycling the unused peroxide or that higher brightness possibly could be obtained economically if the bleaching reaction were given more time. Perhaps sodium silicate, magnesium sulfate, or some other reagents could be added to the pulp slurry, either before or after the cooker. Discharging the process stream into a bleach tower might lead to more effective use of the peroxide. However, recycling of unused bleaching reagent, along with unused sodium hydroxide, appears to be the more attractive option for reducing chemical and processing costs.

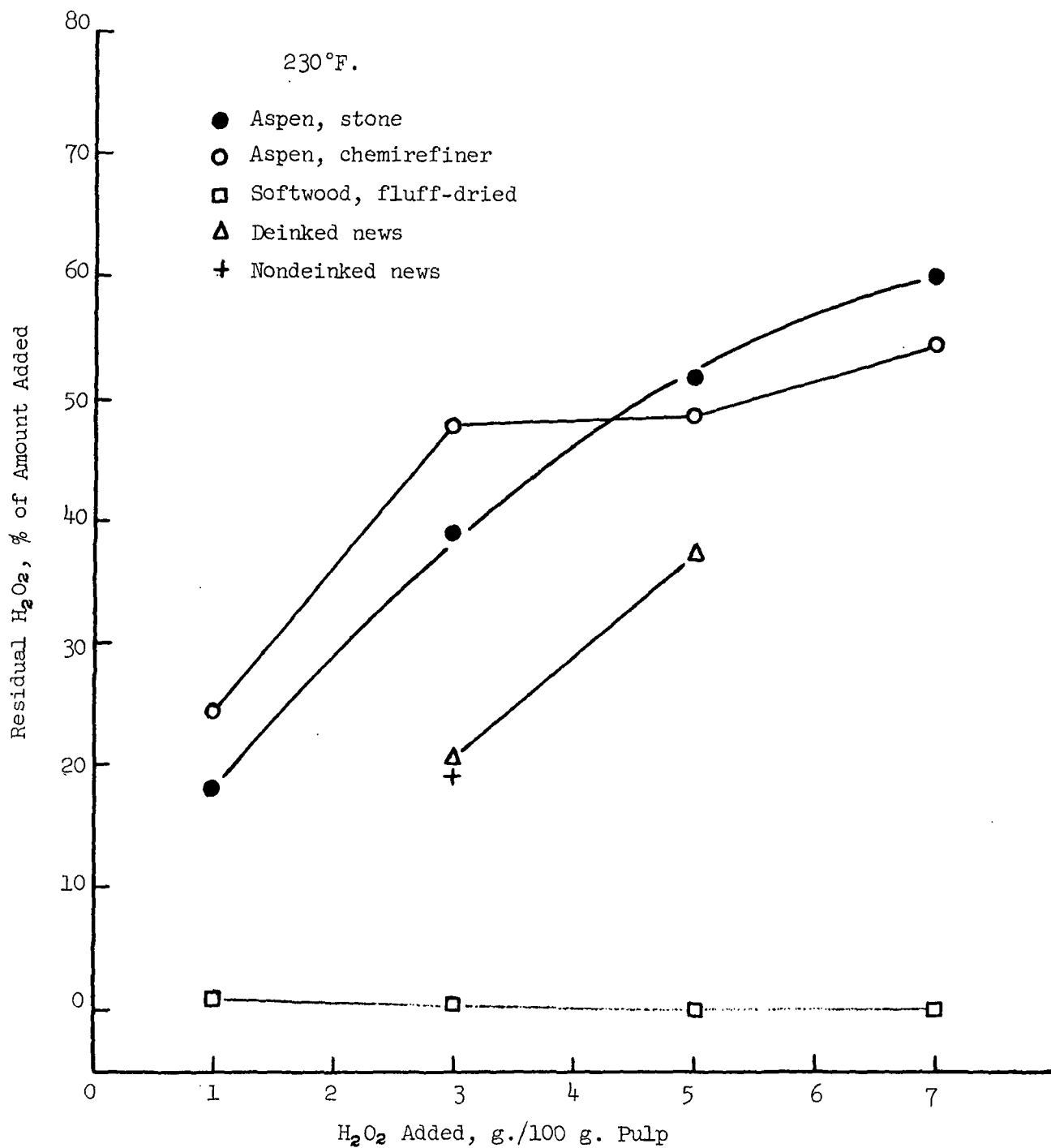


Figure 4. Hydrogen Peroxide Remaining After Treating Pulps at 230°F. with 10% NaOH

The 73.3% brightness for the aspen stone groundwood treated with 7% peroxide, can now be viewed in a different way. Since 60% of the peroxide added is not used, only 40% or 2.8 g. per 100 g. o.d. pulp was consumed in raising the brightness 24.4 points or 8.7 points per percent peroxide consumed. The treatment with 5% peroxide, 48% consumed, produced 7.8 points per percent reacted and with 3% peroxide, 61% consumed, gave 10.6 points brightness per percent reacted. Similar bleaching increments are also obtained with the chemirefiner pulp.

If the residual peroxide can be reused, then combined bleaching and bonding improvement appears to be economically sound.

The fact that there is no residual peroxide with the softwood market pulp indicates that there is some unknown factor associated with this pulp. As seen in Fig. 4, there is residual peroxide for the reclaimed newsprint treatments. Since that pulp also is, mainly, northern softwood groundwood (see Appendix) it is unlikely that the absence of peroxide in the treated market pulp is typical of softwood pulps.

### Opacity

The opacity of the mixed furnish handsheets is plotted in Fig. 5 to 7 as a function of the processing conditions. Increasing amounts of both caustic and peroxide reduce the opacity of the hardwood handsheets. The loss with the peroxide follows the higher brightness values and makes the 80% groundwood handsheets more like the 100% kraft roughly in proportion to the changes in brightness. The reduced opacity with the caustic alone, probably is related to the improved bonding discussed in the next section. Part of the lower opacity of the bleached pulps must also be related to this factor.



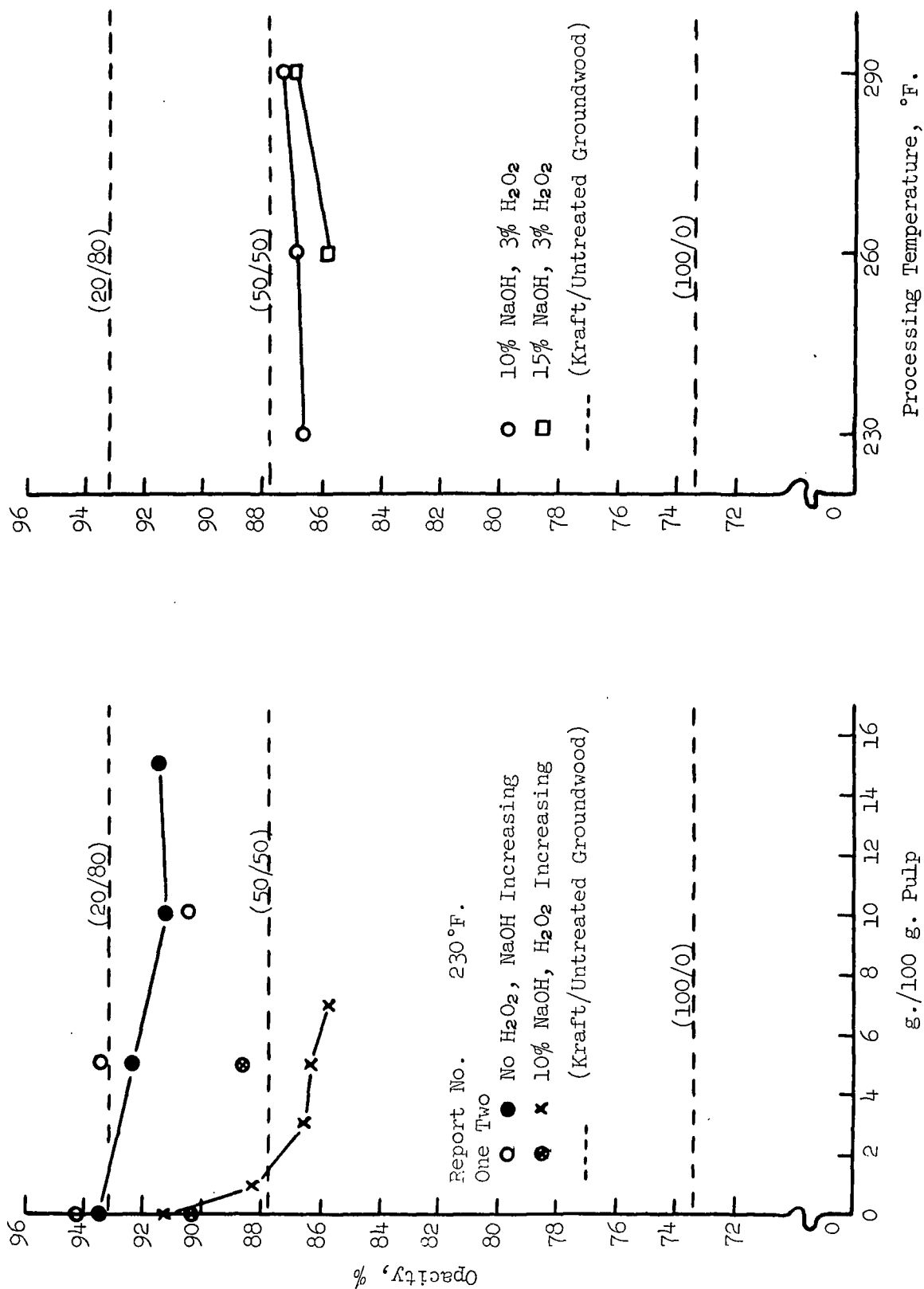


Figure 5. 80% Aspen Stone Pulp: Opacity vs. Treatment

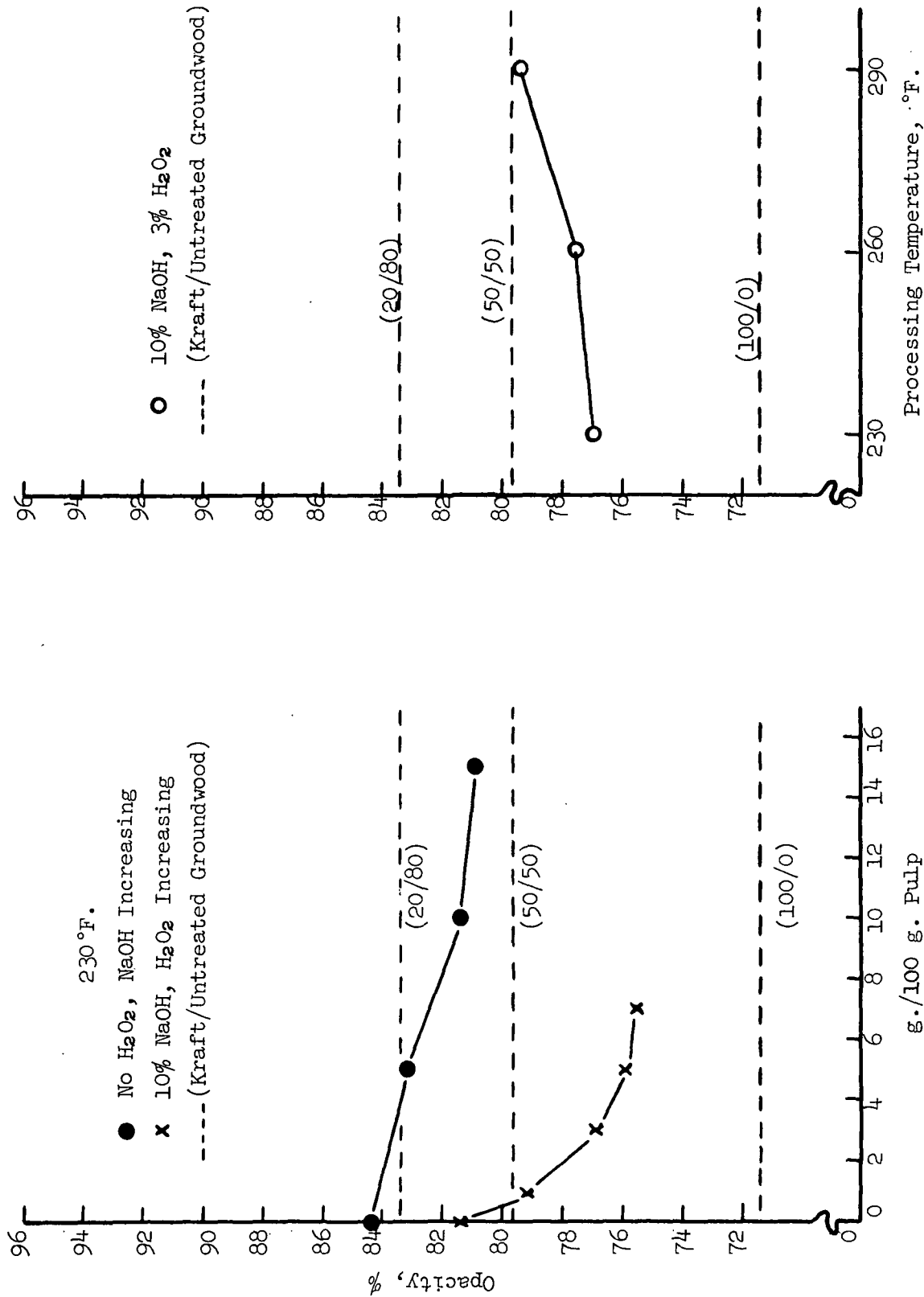


Figure 6. 80% Aspen Chemirefiner Pulp: Opacity vs. Treatment

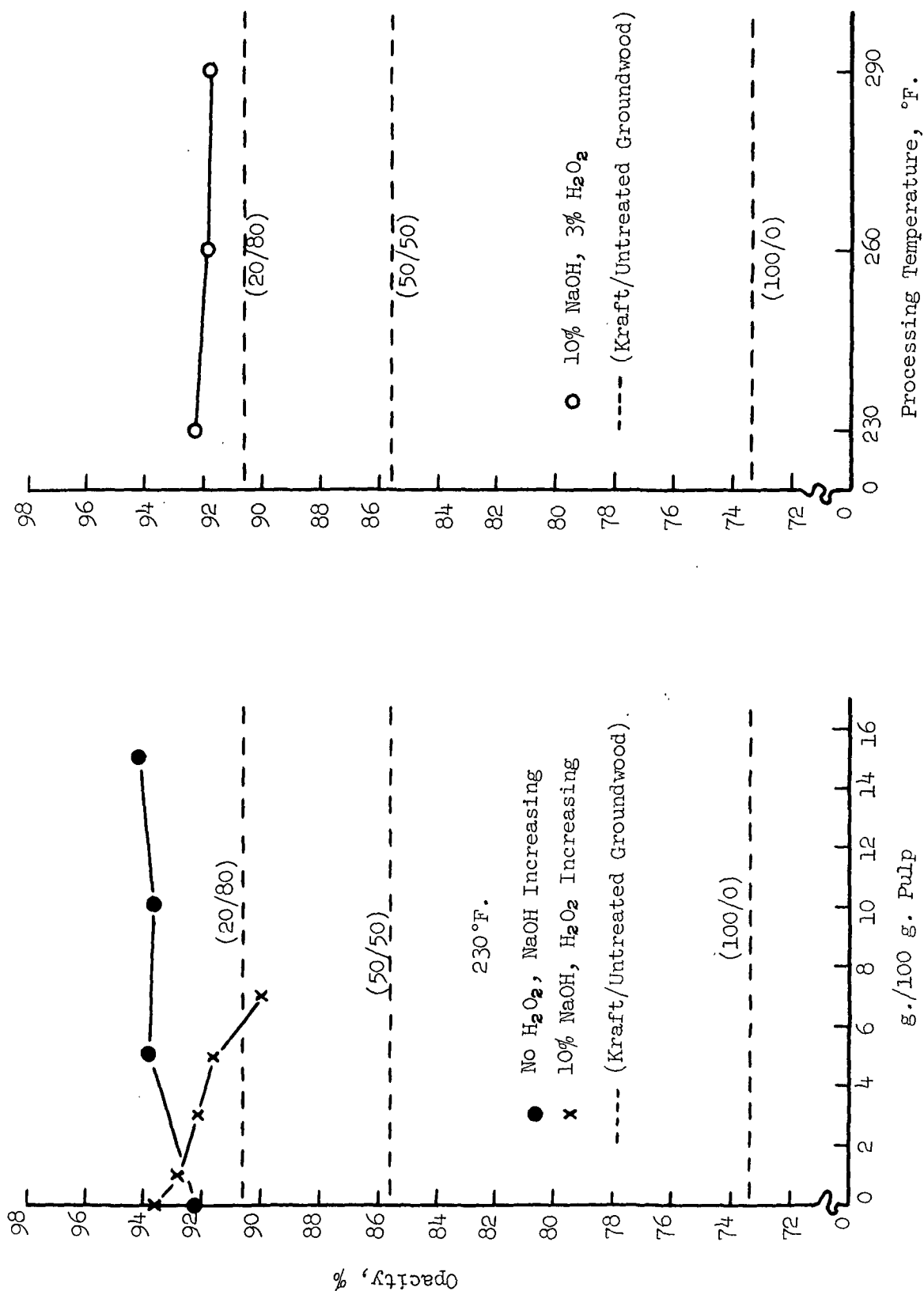


Figure 7. 80% Softwood Pulp: Opacity vs. Treatment

The softwood market pulp shows higher opacity as the sodium hydroxide concentration is increased. The browning of this pulp may be a factor in this case. The temperature effects seen for all three pulps parallel the brightness trends. That is, the inverse relationship between opacity and brightness one expects, is seen in these data.

### Tensile Strength

Changes in the tensile strength of the 80% groundwood handsheets with changing process conditions are displayed in Fig. 8 to 10. Outstanding improvements are obtained in that property, expressed as breaking length, with the two aspen pulps. The tensile strength of the stone groundwood handsheets almost doubles as the sodium hydroxide concentration is raised to 10% but is not further improved by increasing the concentration to 15%. In contrast, the chemirefiner pulp shows improvement through 15% caustic suggesting that even higher levels might continue to show enhancement. With both pulps, jet-cooking the alkaline pulp suspensions produces bonding capabilities in the treated pulp which give much greater tensile strength from the 80% groundwood furnishes than is obtained with those containing only 50% of the untreated groundwood pulps.

The tensile strength of the handsheets must be affected, in some way, by the properties of the kraft pulp used in the blends. With the untreated groundwood pulps, the tensile strength increases with the amount of kraft pulp in the furnish. However, the furnishes containing 80% chemirefiner pulp treated with 5, 10, and 15% NaOH all have tensile strength values greater than the all-kraft handsheets. It would be extremely interesting to see what tensile values these treated pulps would produce by themselves or blended with a stronger chemical pulp or a small percentage of rayon fibers.

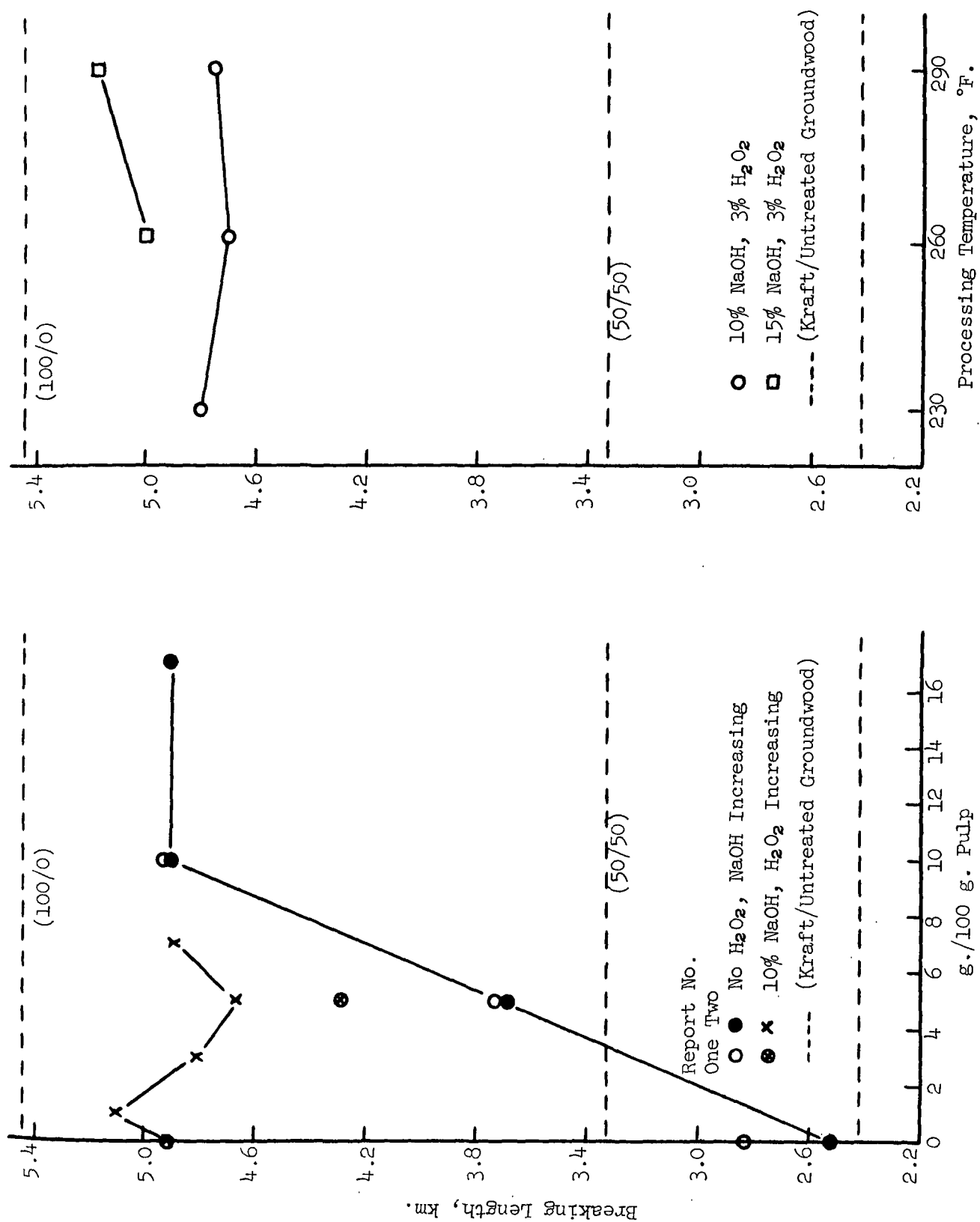


Figure 8. 80% Aspen Stone Pulp: Breaking Length vs. Treatment

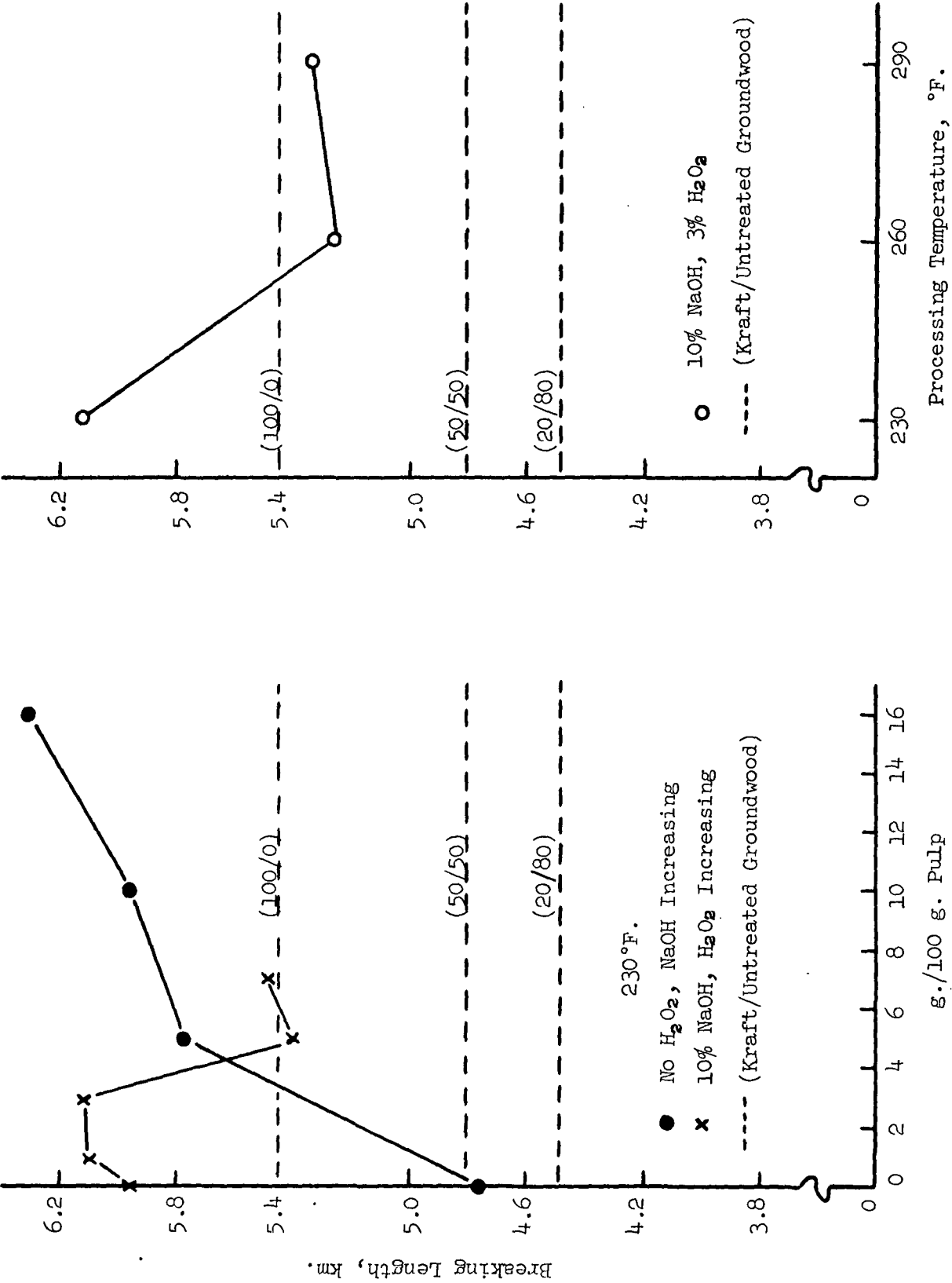


Figure 9 and 10 showing the relationship between breaking length and processing temperature for different pulp treatments.

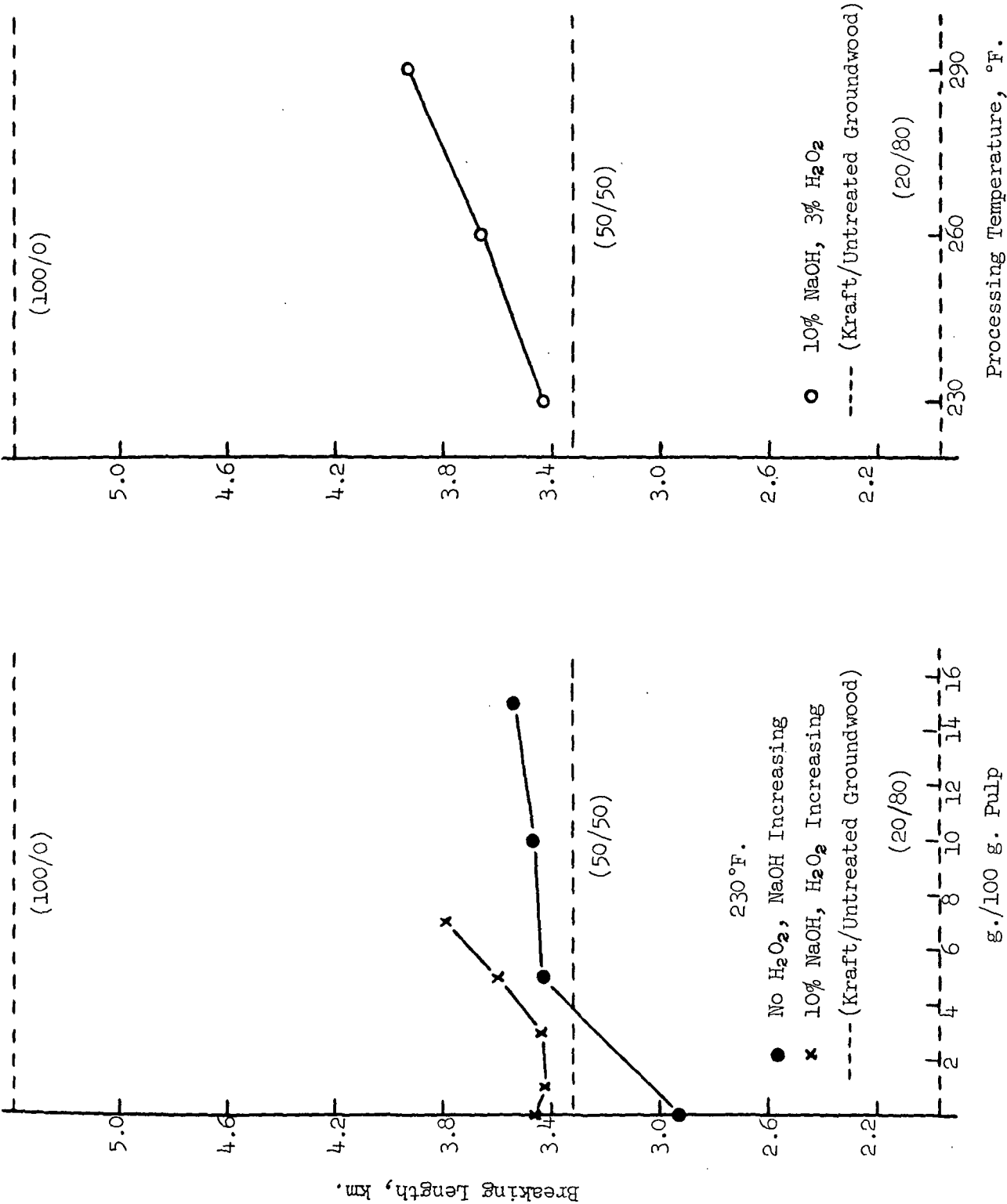


Figure 10. 80% Softwood Pulp: Breaking Length vs. Treatment

On the basis of these results, it should be possible to replace considerable amounts of chemical pulp with treated groundwood pulp to maintain or improve tensile strength while increasing opacity (see Fig. 5 and 6 vs. 8 and 9).

The chemirefiner pulp responds to jet cooking without caustic to the extent that the 80% groundwood furnish matches the tensile strength of the 50% unheated groundwood blend. This represents a change of about 6% (similar to heating the stone groundwood in Report One). If this is "latency," (lower bonding strength due to flash drying or rapid cooling of groundwood specimens drawn from the refiner or stone pit and which is restored by prolonged treatment in hot water in a British disintegrator) then it is also found with the softwood market pulp. Jet cooking that pulp raises the breaking length of the 80% furnish from about 2.0 to 2.8 km. or by 40% (Fig. 10).

The softwood pulp (Fig. 10) does respond to the sodium hydroxide but the greatest improvement is between 0 and 5% with only a gradual increase between 5 and 15% NaOH. The initial enhancement is sufficient to bring the level of tensile strength for the 80% groundwood handsheets above that of the 50% unheated and untreated control.

The bonding ability of these three pulps responds somewhat differently to treatment with hydrogen peroxide. With 10% NaOH at 230°F., the tensile strength of the aspen stone groundwood treated with 1 to 7% peroxide centers on the value obtained without the bleach. This seems to indicate that peroxide bleaching has no great effect upon bonding under these conditions. However, the minimum value does correspond to an even lower value obtained under the same conditions in Report One (see Fig. 8). Since the data for the aspen stone groundwoods used in



Reports One and Two agree in most other respects, there remains some question as to possible harmful effects of peroxide upon aspen stone groundwood bonding.

Raising the processing temperature to 260 and 290°F. has little effect upon the tensile strength of the stone pulp with the 10% caustic and 3% peroxide treatments (Fig. 8). When 15% sodium hydroxide is used with that amount of peroxide, higher tensile strengths are obtained and the value increases as the processing temperature is raised from 260 to 290°F. Since both values are higher than the 230° processing without peroxide, it appears that peroxide and more heat improve bonding with 15% NaOH.

Peroxide concentrations above 3% reduce the tensile strength of the 80% chemirefiner and 20% kraft pulp handsheets to values like those from the all-kraft handsheets. Even so, the 80% groundwood furnish using pulp treated with 10% NaOH at 230°F. has much greater opacity (Fig. 6) than the kraft handsheets; however, the brightness is lower. Higher processing temperatures reduce the tensile strength. Thus, high peroxide concentrations and high processing temperatures (i.e., above 230°F.) with peroxide reduce the tensile strength of jet/alkali processed aspen chemirefiner groundwood.

In contrast with the refiner pulp, the softwood groundwood bonding is improved by high peroxide concentrations and higher processing temperatures (Fig. 10). The fact that the bonding level increases with the severity of the treatment suggests softwood pulps need more drastic treatments than the hardwood groundwoods. It is possible that bonding improvement depends upon delignification of the groundwood fiber surfaces. If so, then a number of chemical combinations suggest themselves for further experimentation for improved softwood pulp bonding.

### Tear Factor and Tensile Energy Absorption

The runnability of printing paper rolls (freeness from web breaks during printing) is predicted by either the paper's tearing resistance or tensile energy absorption test values according to the market experience of the manufacturer. Even though furnishes containing greater amounts of treated groundwood and lesser amounts of chemical pulp may equal the tensile strength requirement of a standard furnish, the concern for runnability will also affect how much chemical pulp can be replaced by treated groundwood. Other performance requirements of paper are also related to tearing resistance, but in mixed furnishes containing groundwood, runnability is likely to be of greater concern. Thus, both the tear factors and tensile energy absorption values are considered together in the same section of this report.

Improved bonding through pulp refining techniques or by using internal adhesives usually reduces tearing resistance. Thus, the fact that the different jet/alkali processing treatments given the two hardwood pulps had practically no effect upon the tearing resistance (see Fig. 11 and 12) has positive rather than negative significance. However, if runnability predictions are based upon the tear factor of a 50% untreated groundwood furnish, then an 80% treated groundwood furnish would not be able to meet this standard. The small improvement in tear for the softwood groundwood (Fig. 13) has little immediate significance in view of the generally low tensile strength levels obtained with this pulp (Fig. 10).

On the other hand, if tensile energy absorption values are used to gage runnability, then the jet/alkali processed hardwood groundwoods should be capable of replacing more of the chemical pulp. In Fig. 14 and 15, the tensile energy absorption values of the 80% treated groundwood furnishes approach the

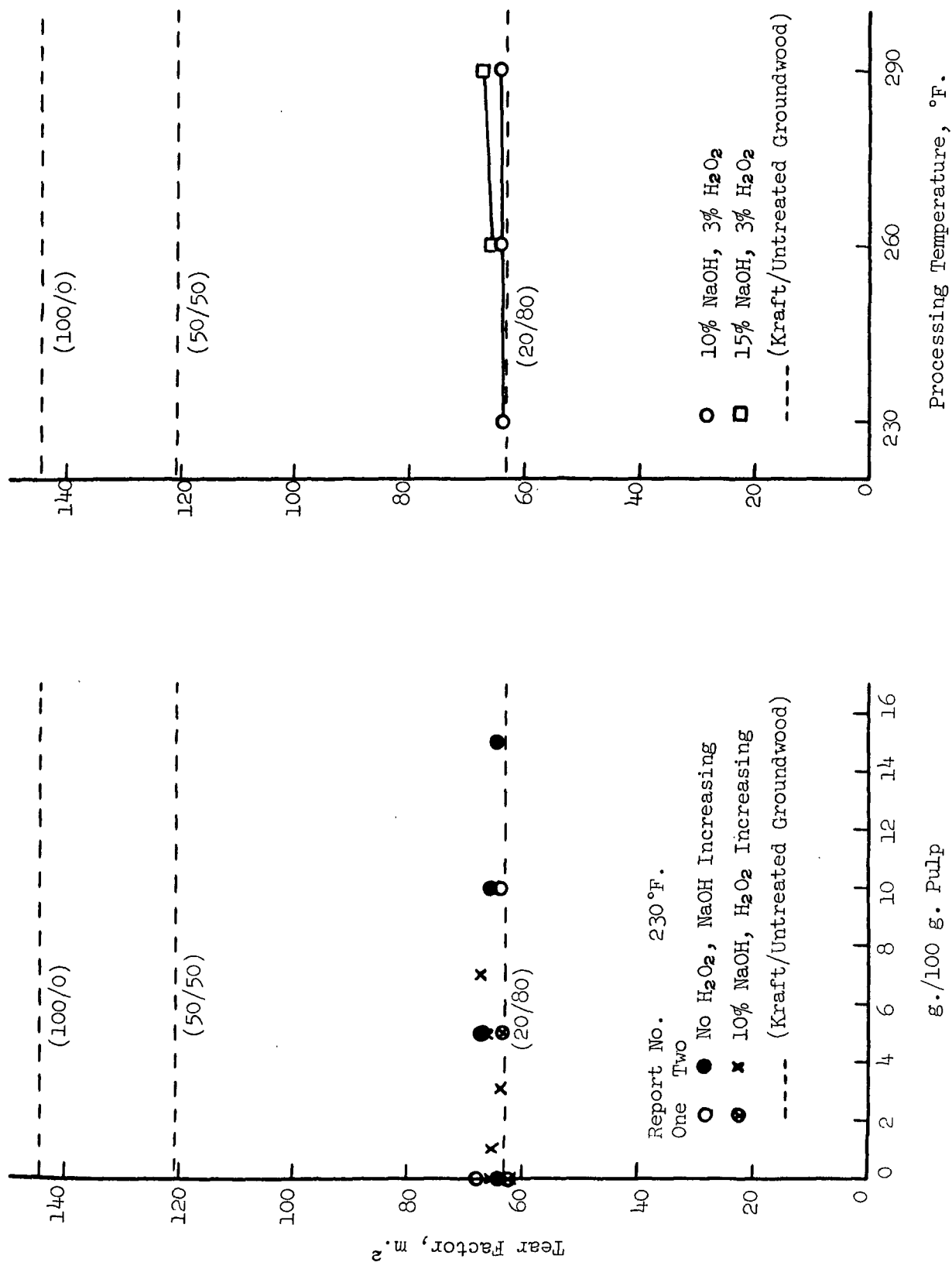


Figure 11. 80% Aspen Stone Pulp: Tear Factor vs. Treatment

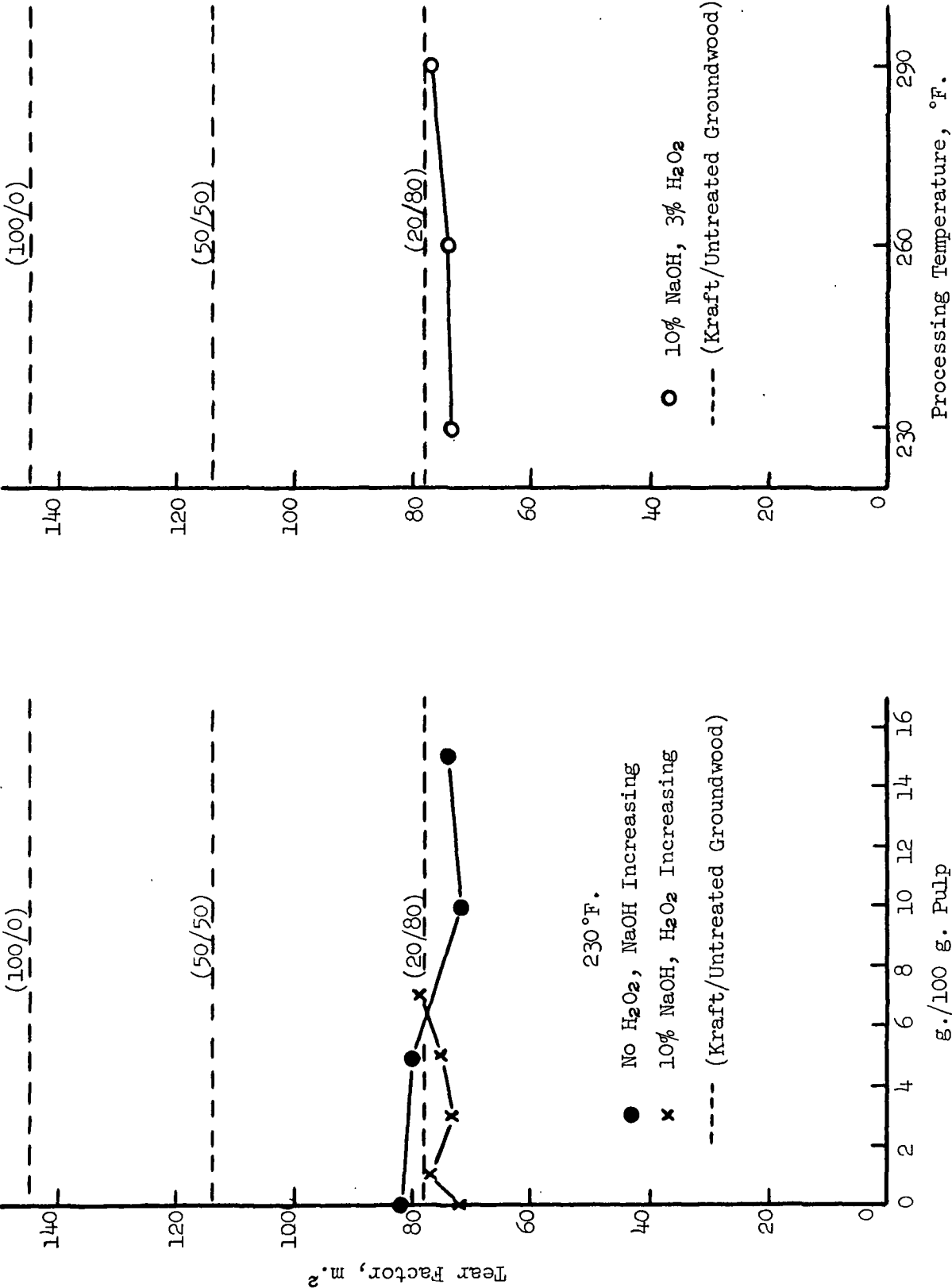


Figure 12. 80% Aspen Chemirefiner Pulp: Tear Factor vs. Treatment

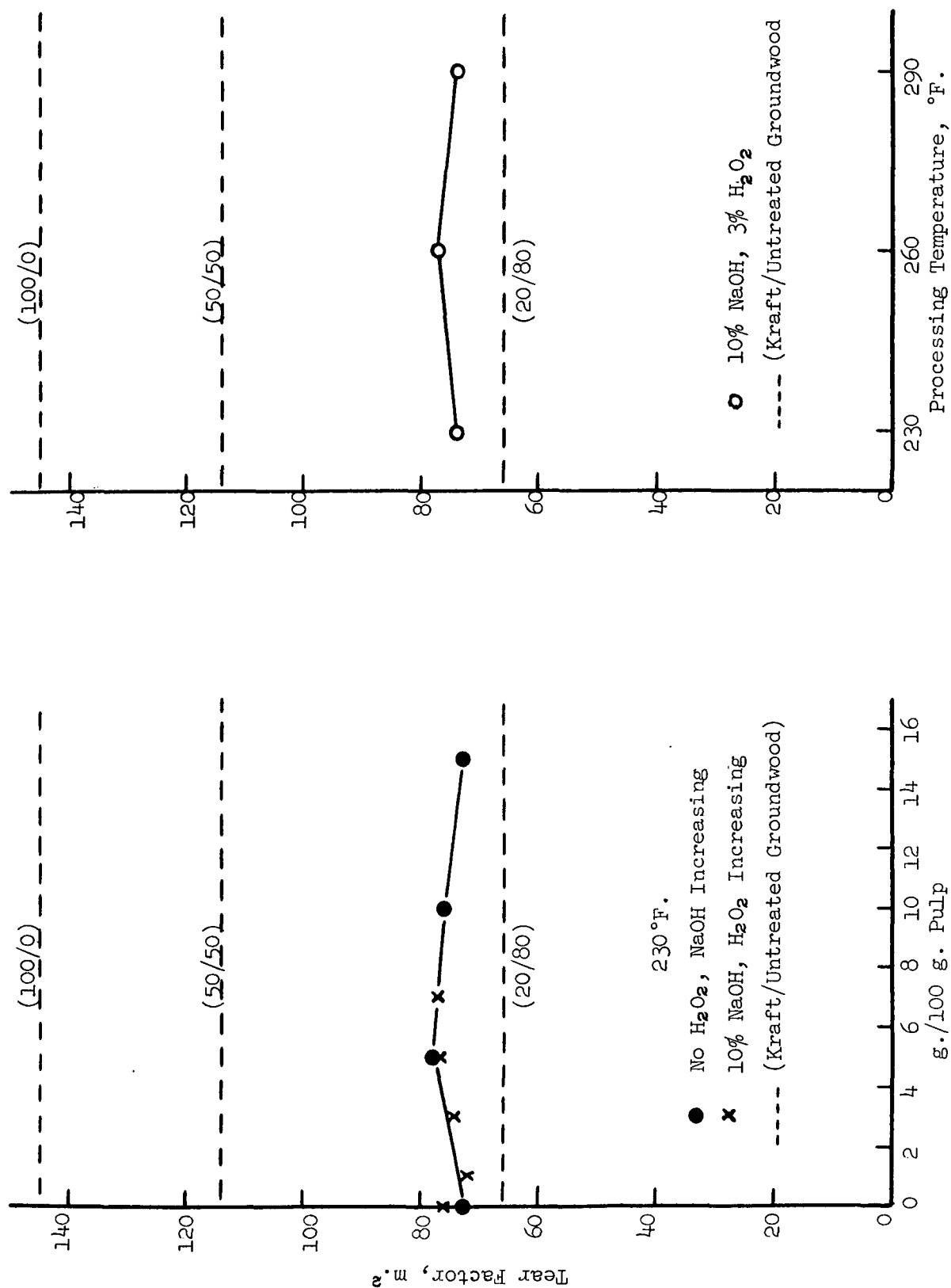


Figure 13. 80% Softwood Pulp: Tear Factor vs. Treatment

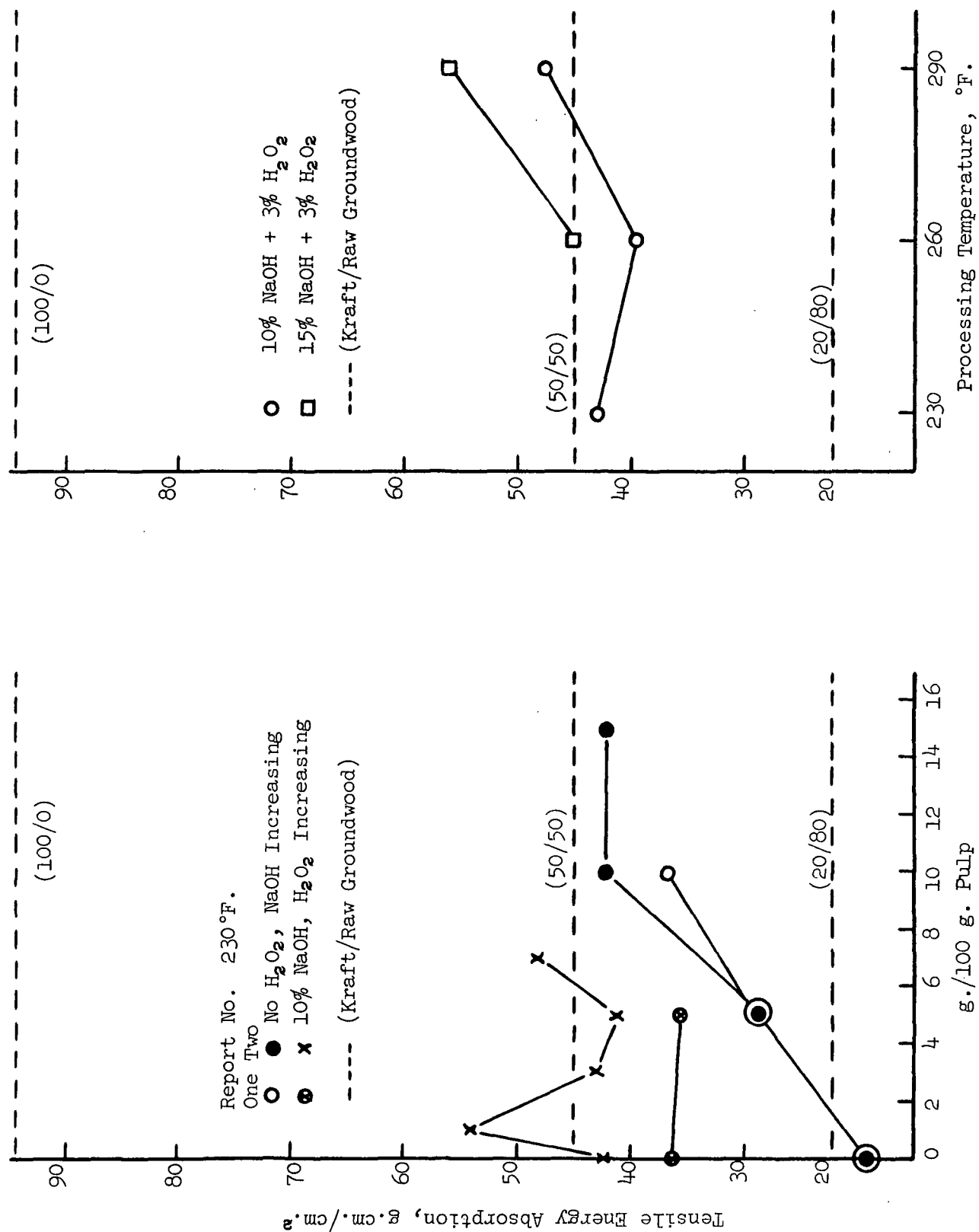


Figure 14. 80% Aspen Stone Pulp: Tensile Energy Absorption vs. Treatment

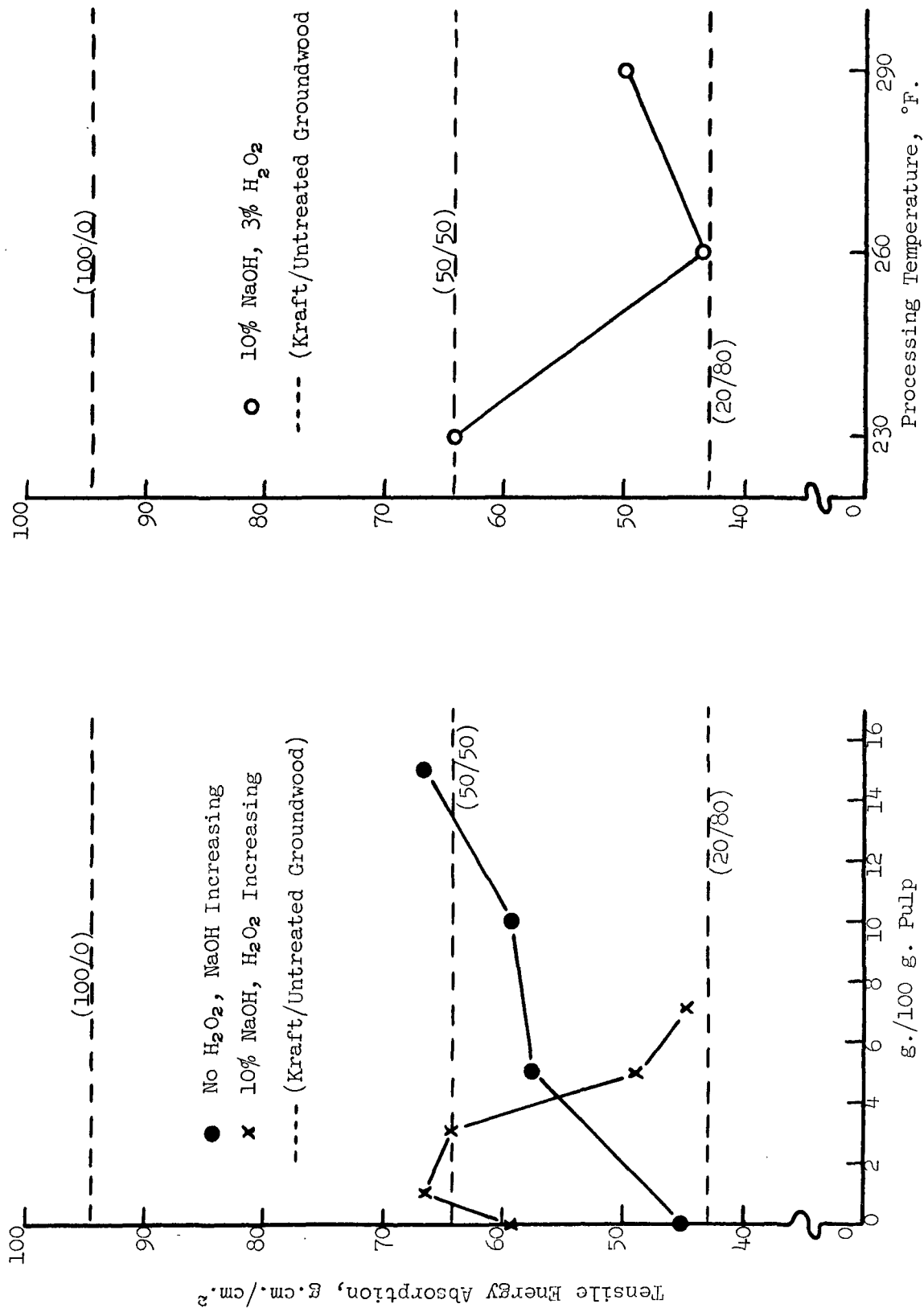


Figure 15. 80% Aspen Chemirefiner Pulp: Tensile Energy Absorption vs. Treatment

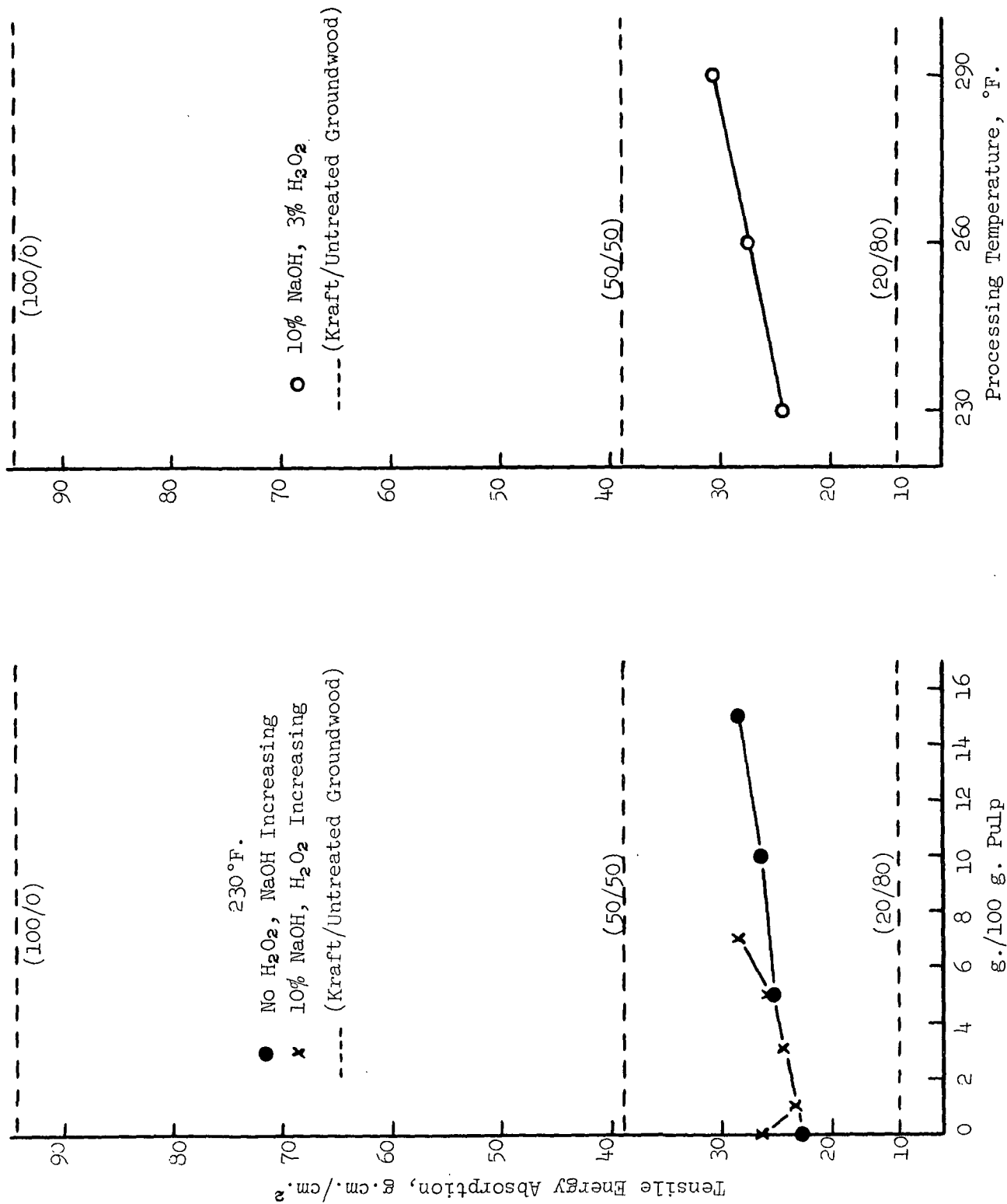


Figure 16. 80% Softwood Pulp: Tensile Energy Absorption vs. Treatment



levels given by the 50% untreated groundwood furnishes. The pattern of the effects of the different processing conditions upon these pulps is like that for tensile strength. However, the maximum values are not as great a percentage of the performance of the all-kraft furnish as they were for the tensile strength.

The commercial softwood groundwood results are not as encouraging, but higher tensile energy absorption values are obtained as the processing conditions become more severe (Fig. 16). This follows the pattern seen for the tensile strength of these furnishes (Fig. 10). The positive aspect of these results lies in the clues they give for further efforts to improve softwood bonding.

#### Tensile Stiffness

The tensile stiffness of the trial handsheets is plotted in Fig. 17 to 19. This parameter is derived from the slope of the linear portion of the stress-strain curve used to determine the tensile strength and tensile energy absorption values, and is a function of the modulus of elasticity and the thickness of the specimen. The response patterns in the figures just noted are like those for tensile strength (Fig. 8 to 10). The main differences are in the levels of the values from the trial papers. The aspen stone groundwood treatments produce 80% groundwood handsheets having values greater than the all-kraft controls as the caustic concentration is raised (Fig. 17). Increasing amounts of peroxide lower the tensile stiffness of the 10% NaOH treatment while higher processing temperatures have little or no effect over the range of 230 to 290°F. The same type of response is seen with the chemirefiner hardwood (Fig. 18). Here, the major point of difference between tensile strength (Fig. 19) and tensile stiffness is the lack of a strong response to processing temperature

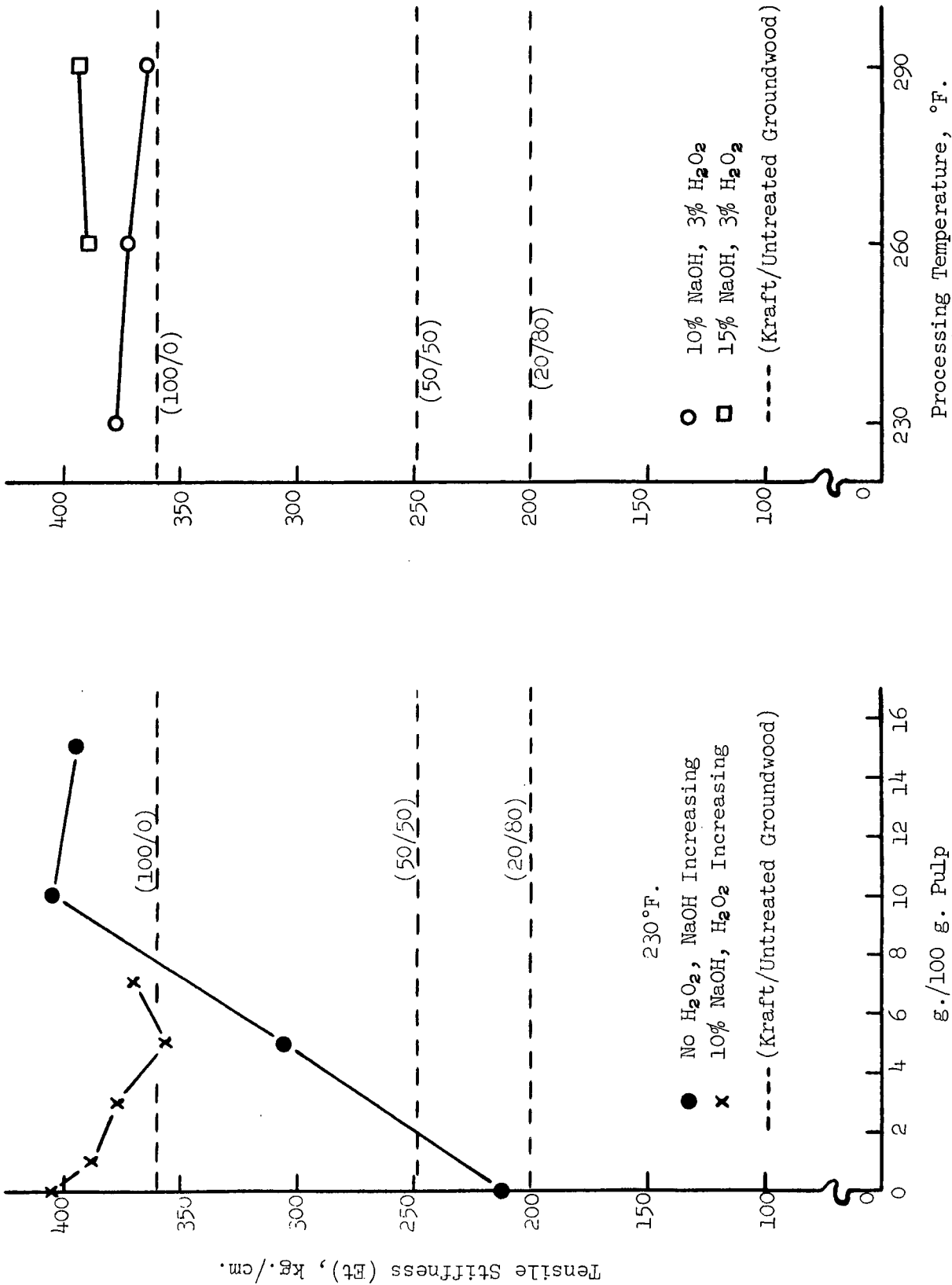


Figure 17. 80% Aspen Stone Pulp: Tensile Stiffness vs. Treatment

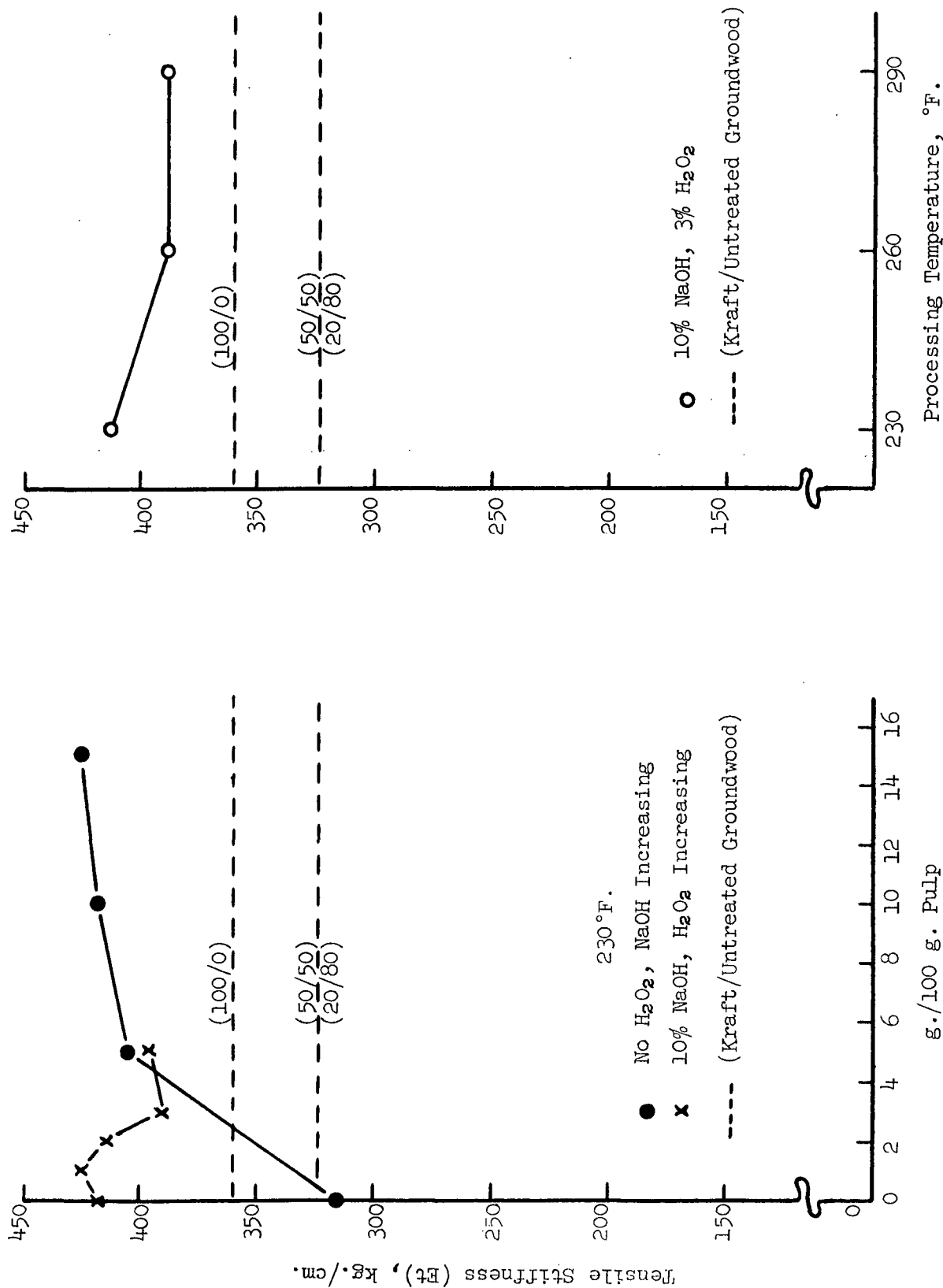


Figure 18. 80% Aspen Chemirefiner Pulp: Tensile Stiffness vs. Treatment

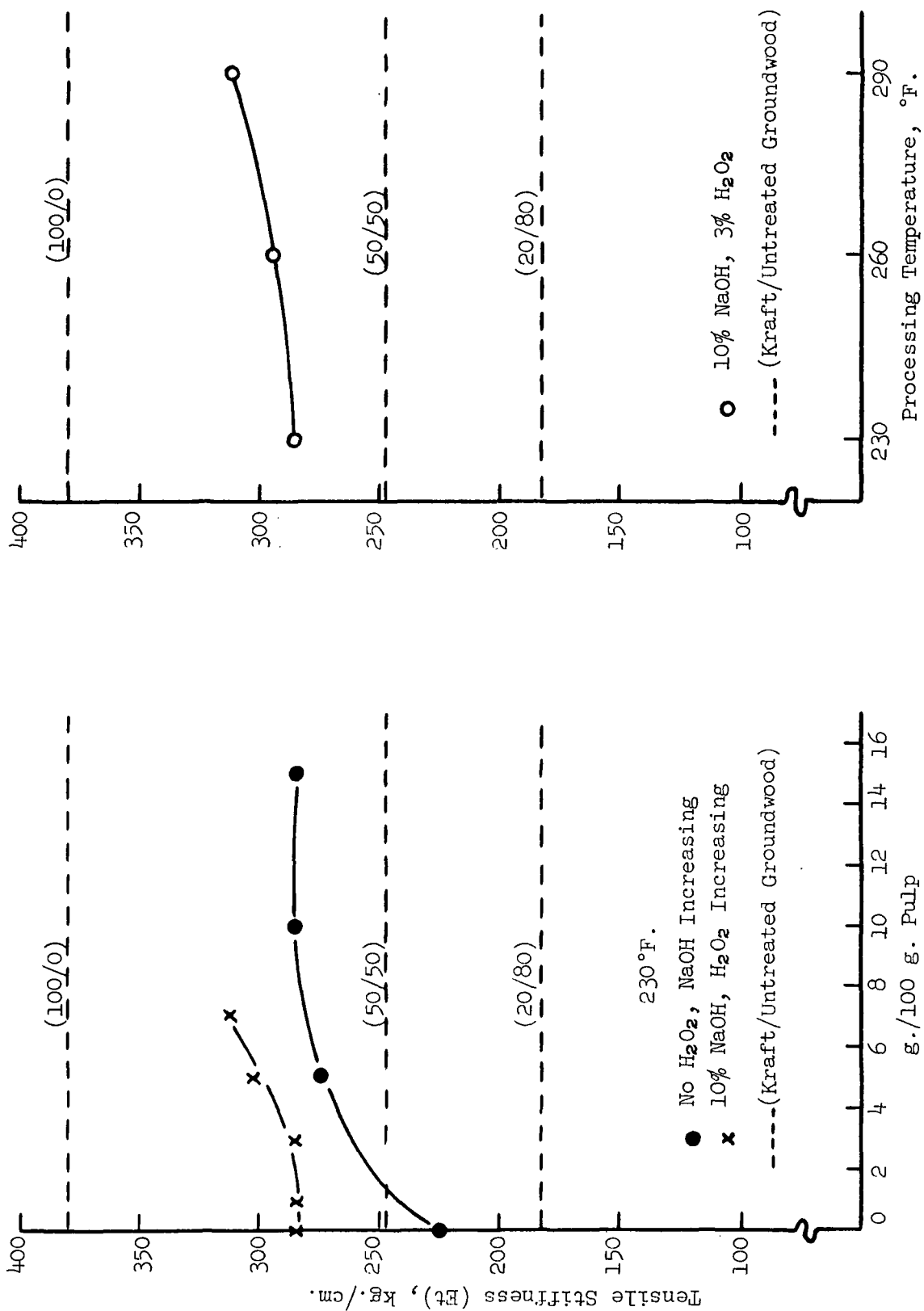


Figure 19. 80% Softwood Pulp: Tensile Stiffness vs. Treatment

in the stiffness data. The softwood groundwood pulp shows greater response to the treatment conditions (compared with the untreated controls) for tensile stiffness than for any of the other properties tested.

The significance the higher tensile stiffness values for the jet/alkali process is not clear. Paper produced from these pulps should be less flexible but not necessarily have lower fold. Experience in this laboratory has been that higher tensile stiffness is produced by increasing amounts of chemical fines in the furnish. This is consistent with the proposition that the jet/alkali treatments are removing lignin from the fines by alkaline pulping reactions.

#### Porosity and Apparent Density

The data for the Bendtsen air permeation rate (Fig. 20 to 22) and apparent density (Fig. 23 to 25) are related in the expected pattern that the less porous sheets have the highest density. Both hardwood pulps produce papers which have air permeation rates considerably lower than the all-kraft paper but their apparent density is lower than that reference paper. Apparently, the jet/alkali process produces a greater number of small pores without reducing the sheet volume to that of the kraft sample. Reduced pore size (lower air permeation rate) along with lower density may suggest improved letterpress printability and lower ink consumption.

The conditions leading to higher density also produce higher tensile strength. However, this generalization cannot be used to compare one kind of pulp with another. The hardwood pulps have unequal tensile strength at about the same density.

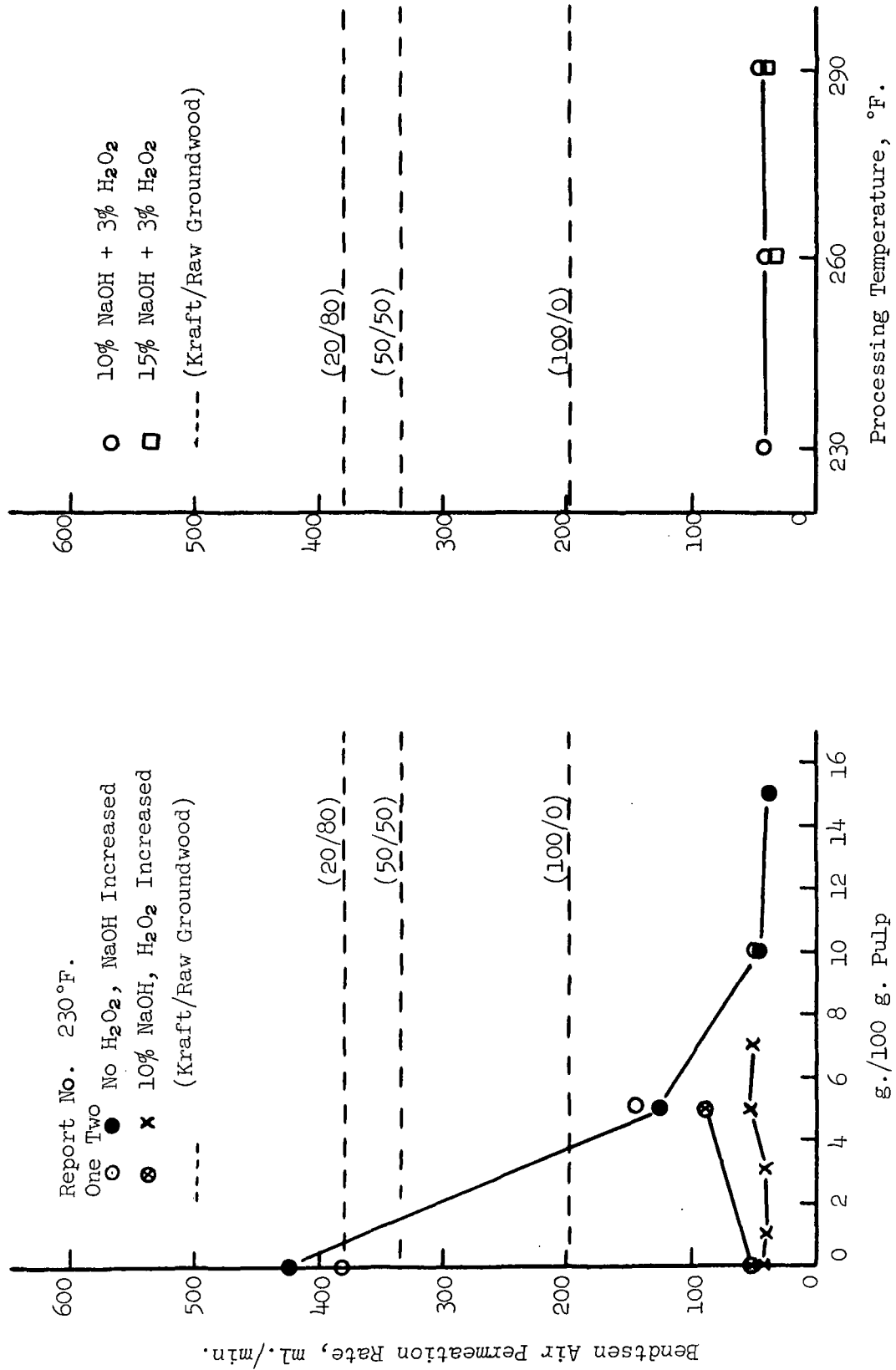


Figure 20. 80% Aspen Stone Pulp: Porosity vs. Treatment

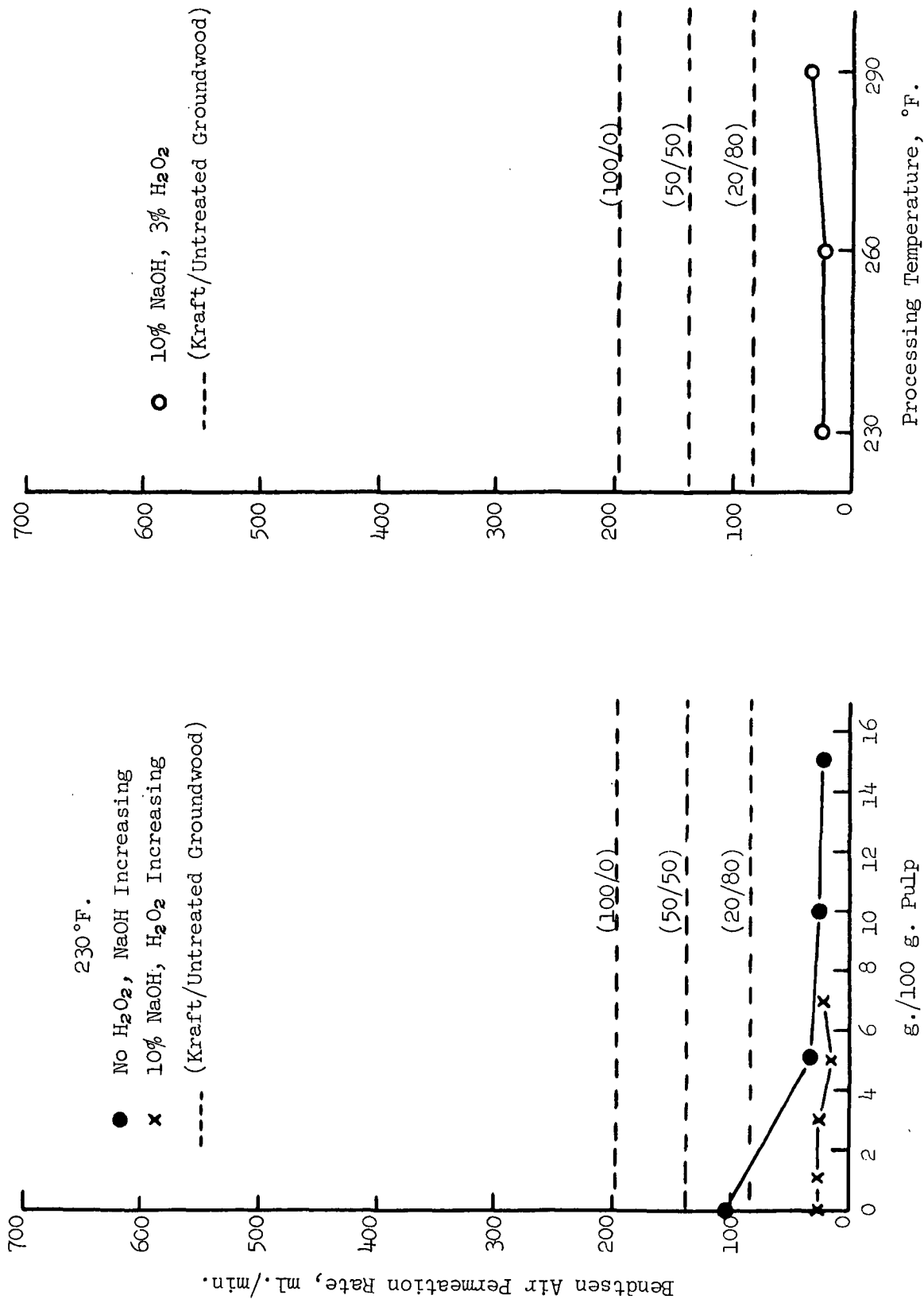


Figure 21. 80% Aspen Chemirefiner Pulp: Porosity vs. Treatment

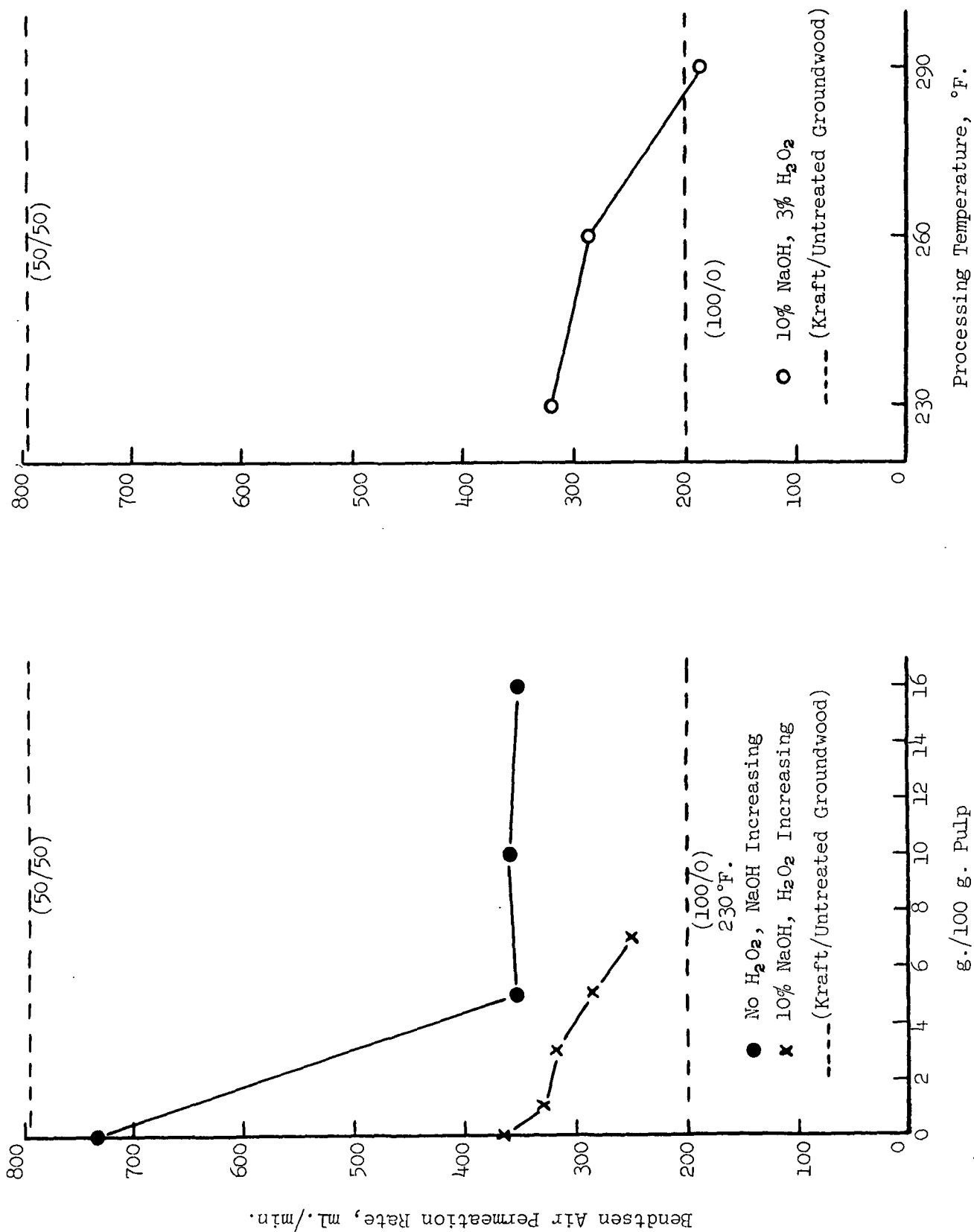


Figure 22. 80% Softwood Pulp: Porosity vs. Treatment



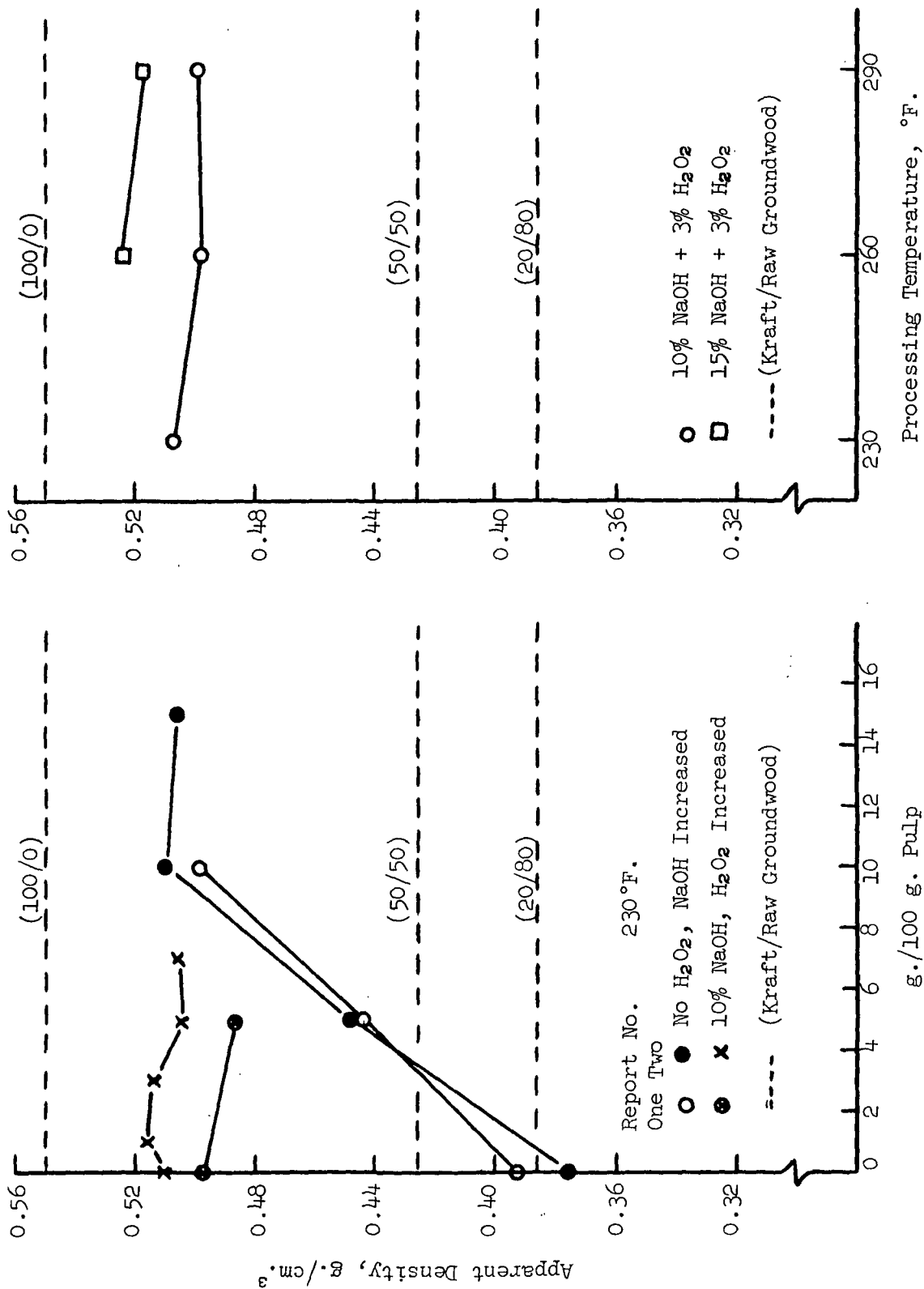


Figure 23. 80% Aspen Stone Pulp: Density vs. Treatment

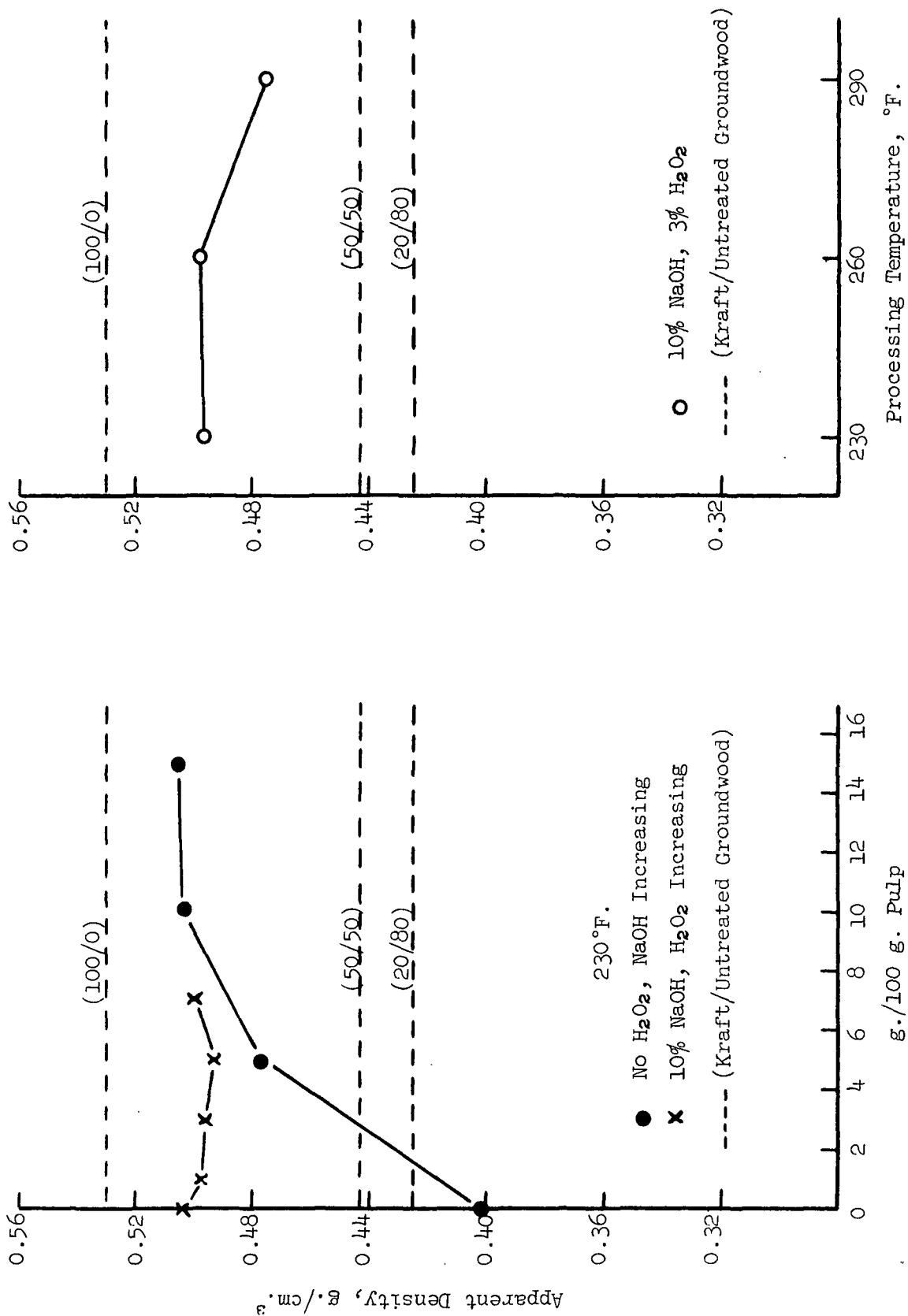


Figure 24. 80% Aspen Chemirefiner Pulp: Density vs. Treatment

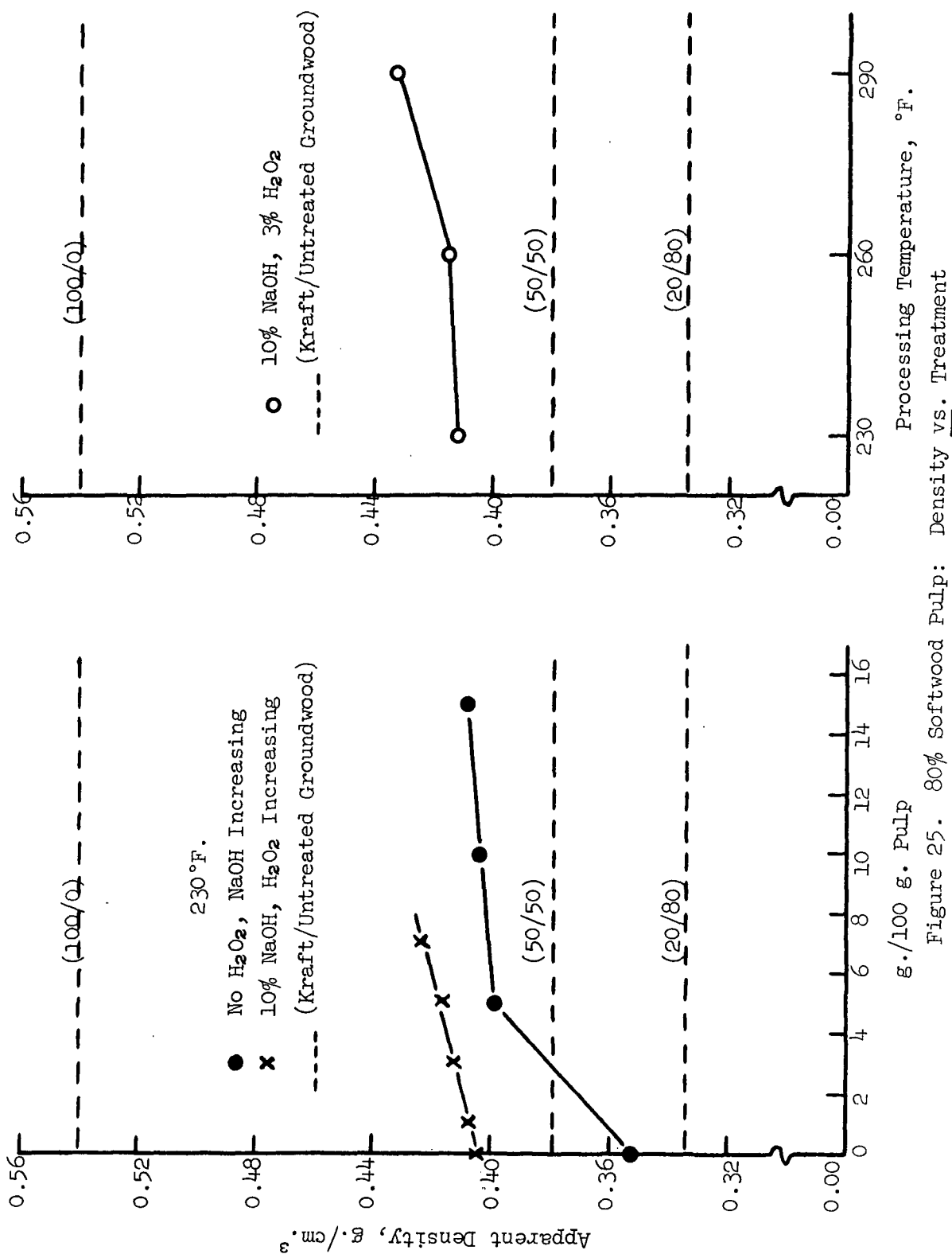


Figure 25. 80% Softwood Pulp

The softwood market groundwood follows the same pattern of responses as the aspen stone groundwood but to a lesser degree as expected from the lower bonding improvement.

The major difference among the three pulps lies in the initial condition of the chemirefiner pulp and its effect upon porosity. Blending the untreated stone hardwood and the market softwood pulps with the kraft produces a more porous and less dense paper as the groundwood proportion of the furnish increases. In contrast, the untreated chemirefiner pulp blends become less dense and less porous as the groundwood increases in the furnish. The structure of the paper is assuming a greater volume and a less open structure with increasing amount of this untreated groundwood. Chemical treatment in the jet cooker produces changes which yield a more compact, less open paper just as it does with the other two pulps.

### Freeness

The Canadian Standard freeness values at pH 5 were obtained for both the treated pulps and the 80% groundwood furnishes. These data are shown in Table V. The kraft pulp alone gave a value of 390 ml. Both untreated aspen pulps reduced the furnish freeness while the hardwood pulp raised it to 420 ml. The freeness of the aspen stone groundwood is reduced by the treatments to some extent but not with a pattern of great consistency. Heat treatment at 230°F. by itself had no effect. Heat plus alkali reduces freeness but that value remains in the range of 80 to 90 ml. for all variations.

There is a peculiar relationship between the furnish freeness and the stone groundwood pulp freeness. The latter goes from values higher to values lower than the pulp freeness as the NaOH concentration increases. This is not

TABLE V

CANADIAN STANDARD FREENESS VALUES FOR GROUNDWOOD PULPS AND 80% GROUNDWOOD FURNISHES AT pH 5 ( $H_2SO_4$ )

The freeness of aged, dewatered bleached kraft in furnish was 390 ml. CSF when resuspended for 300 counts at 2% consistency in a British disintegrator

NaOH, %	H <sub>2</sub> O <sub>2</sub> , %	Cooking Temperature, °F.	Aspen:Stone Pulp      Furnish	Aspen:Chemirefiner Pulp      Furnish	Softwood Pulp      Furnish	Old Newspaper Furnish	Deinked <sup>a</sup> Newspaper Furnish
Untreated			--	110	--	420	--
0	0	230	110	120	160	180	330
5	0	230	80	80	150	200	--
10	0	230	90	70	150	190	330
15	0	230	80	75	150	200	310
10	1	230	90	60	170	180	--
10	3	230	80	60	150	180	290
10	5	230	85	70	130	165	320
10	7	230	85	65	130	160	--
10	3	260	85	65	120	175	--
10	3	290	60	60	100	130	--
15	3	260	90	70	--	--	--
15	3	290	90	70	--	--	--
10 <sup>b</sup>	0	230	90	75	--	--	--
10 <sup>b</sup>	0	18	95	90	--	--	--
0	0	18	105	120	--	--	--

<sup>a</sup> 75% Softwood groundwood, 25% softwood sulfite with some softwood kraft.

<sup>b</sup> From same pulp suspension.

easily explained since the chemirefiner pulp and the softwood pulp do not show this trend. Further, the chemirefiner pulp which produces the least porous hand-sheets at similar apparent densities yields higher freeness values. One might expect this pulp to reduce the furnish freeness more than the stone pulp just on the expectation of greater mat compressibility.

The chemirefiner pulp freenesses are not changed by the treatments but the furnish freenesses are. The furnish freeness decreases with increasing amounts of alkali but is relatively unaffected by peroxide or processing temperature. The freenesses of the softwood groundwood pulp suspensions and 80% groundwood furnishes do not seem to be related in any predictable way except that the furnish freenesses are always higher. The lowest freeness for both the pulp and the furnish does occur for the treatment giving the highest tensile strength. That is, with 10% NaOH/3% H<sub>2</sub>O<sub>2</sub> at 290°F. For the other conditions, freeness does not appear to be a good indicator of potential performance.

#### OLD NEWSPRINT TREATMENTS

Both deinked and nondeinked versions of reclaimed newspapers were treated by the jet/alkali process. Not all the conditions tested with the virgin pulps were attempted in order to be able to evaluate the effect of sodium hydroxide on both forms of the reprocessed groundwoods. The newspapers used happened to be almost entirely from northern softwood pulps. This was determined by microscopic analysis. The deinked pulp, representing about 71% yield, contained 75% softwood groundwood along with a trace of hardwood species (less than 5%), 20% unbleached softwood sulfite, and 5% bleached softwood kraft pulp. The furnish composition thus is not greatly different than that used to test the virgin pulps. The more important difference is that the reclaimed chemical pulps were also treated by the

jet/alkali process, along with the reclaimed groundwood, while the chemical pulp used in the earlier examples was not so treated. It is not known whether chemical pulps will or will not respond to the jet/alkali process. The preparation of each reclaimed pulp is given in more detail in the Appendix.

The handsheet data are given in Table VI and illustrated in Fig. 26 to 33. There is little effect upon the brightness or opacity for the nondeinked pulp by either sodium hydroxide or hydrogen peroxide at 230°F. (Fig. 26 and 27) while brightness is reduced by NaOH and raised by peroxide with the deinked pulp. The deinked opacity is lower than that of the nondeinked pulp, as would be expected, and is unaffected by increasing amounts of sodium hydroxide. Bleaching with peroxide lowers the opacity of the deinked pulp.

The tensile strength of the deinked pulp is increased linearly by adding NaOH and has not leveled off at the 15% addition rate (Fig. 28). In contrast, the nondeinked pulp loses tensile strength as the sodium hydroxide concentration is raised from 5 to 10 and up to 15% on the dry weight of the pulp. The tensile strength of the handsheets from nondeinked pulps treated with 5% NaOH is about the same as that from the deinked pulp jet-cooked without the caustic. The nondeinked pulp control, which would have helped in deciding whether or not the 5% NaOH treatment had any value, was not run. At the time, it was felt that the suspension of old newspapers, which had been beaten for only 300 counts in the British disintegrator, could not be safely pumped through the Moyno pump without the lubricating effect of the caustic. The presence of increasing amounts of peroxide in the 10% NaOH treatment has little effect upon the tensile strength of the deinked pulp but does appear to improve that of the nondeinked form with the single concentration tested.

TABLE VI  
RECLAIMED NEWSPAPERS: HANDSHEETS FROM 100% RECLAIMED FURNISH

Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature, °F.	Pulp Brightness, %	Paper Brightness, %	Opacity, %	Density, g./cc.	Tear Factor, m. <sup>2</sup>	Breaking Length, cm.	TEA, g.cm./cm. <sup>2</sup>	Stretch, %	Tensile, kg./cm.	Bendtsen Air Permeation Rate, ml./min.	Basis Weight, g./m. <sup>2</sup>
Nondeinked														
119	5	0	230	38.1	39.3	99.4	0.414	57.4	3.53	25.7	1.7	284	288	62.5
120	10	0	230	40.0	40.7	98.8	0.392	64.5	3.19	24.5	1.8	260	603	62.0
121	15	0	230	39.3	40.8	98.6	0.388	62.6	3.01	21.5	1.7	251	686	62.8
122	10	3	230	43.1	44.7	98.3	0.410	60.8	3.32	24.3	1.7	278	346	63.5
Deinked														
127	0	0	230	49.6	50.0	95.0	0.376	72.3	3.55	31.2	2.0	273	932	63.2
123	10	0	230	43.9	44.6	95.4	0.408	71.0	4.00	34.9	2.0	304	605	62.8
124	15	0	230	43.2	43.4	95.3	0.403	72.9	4.26	43.9	2.4	298	577	62.4
125	10	3	230	52.0	53.2	91.2	0.406	72.1	3.90	30.5	1.8	316	600	63.4
126	10	5	230	54.0	54.9	91.2	0.408	71.3	3.98	36.1	2.0	314	630	64.1



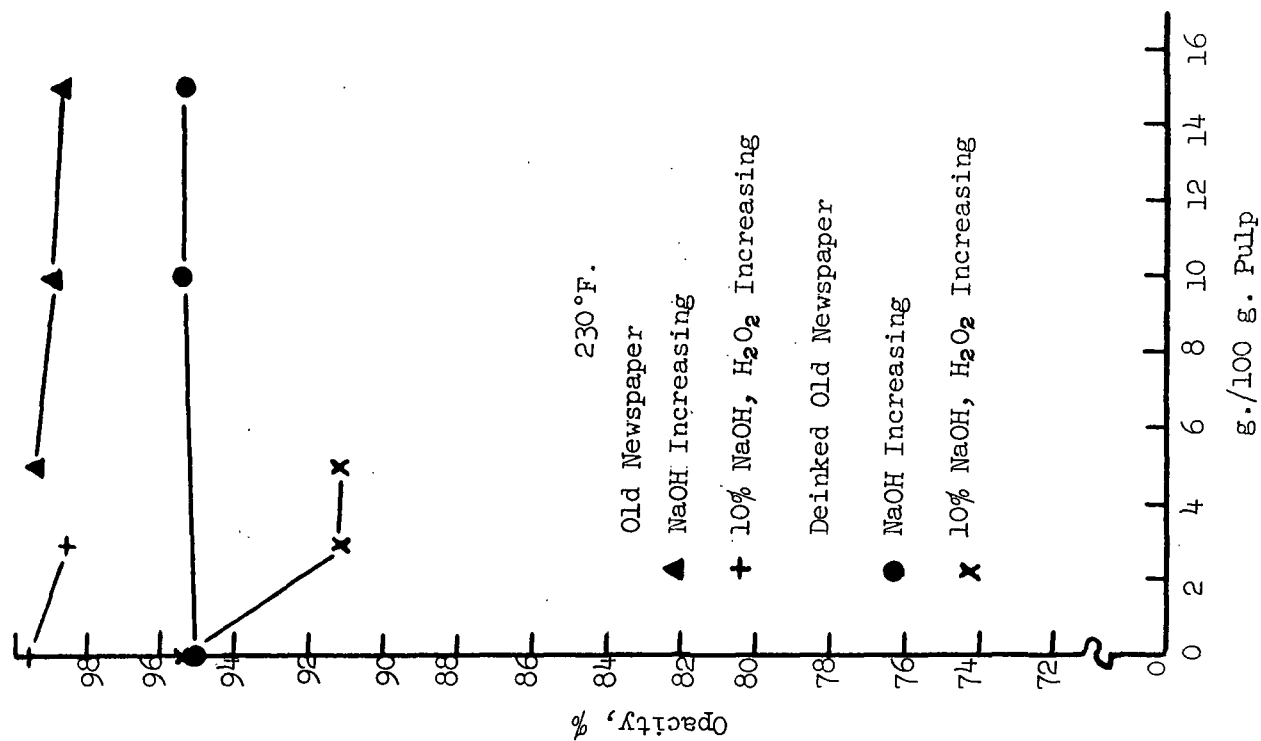


Figure 27. Opacity vs. Treatment

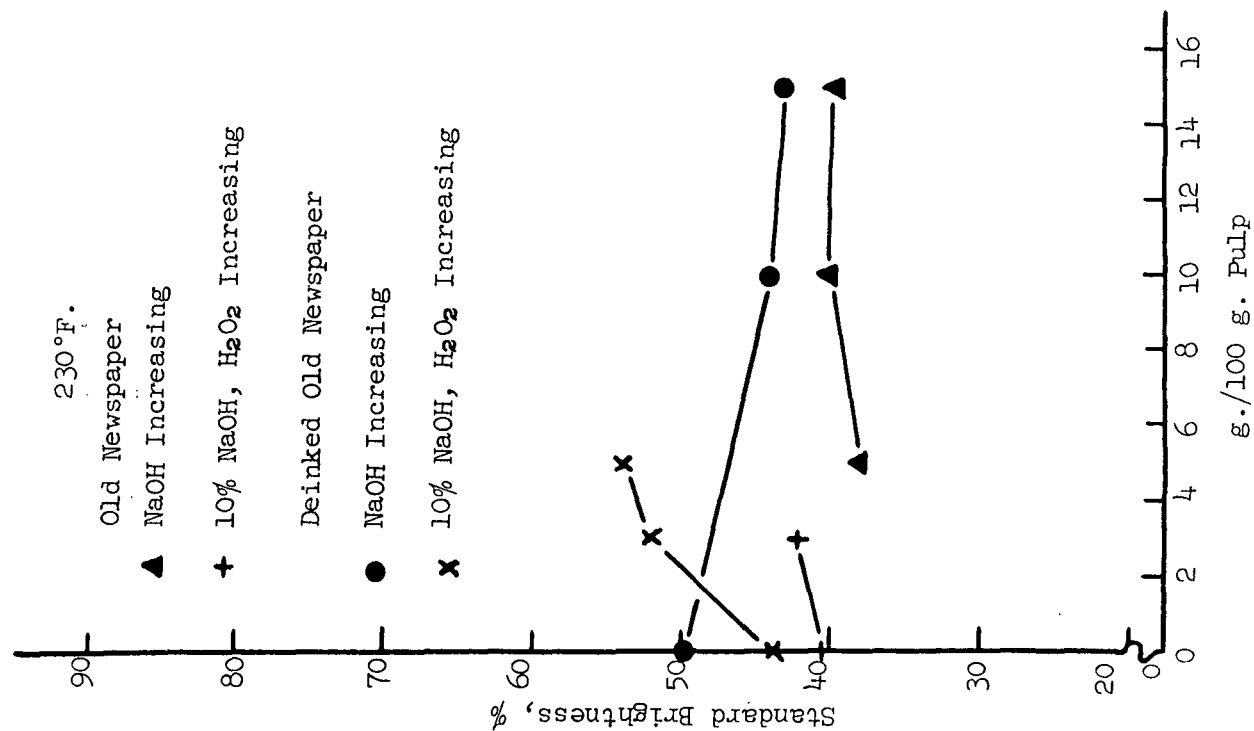


Figure 26. Brightness vs. Treatment

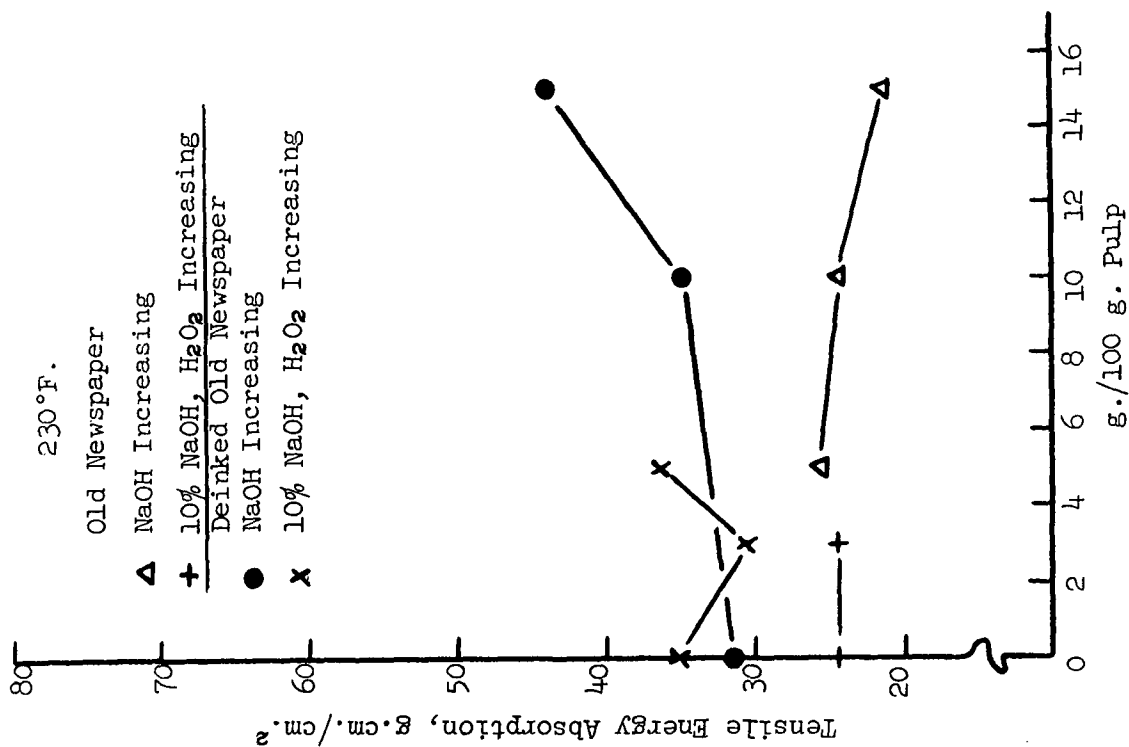


Figure 29. Tensile Energy Absorption vs. Treatment

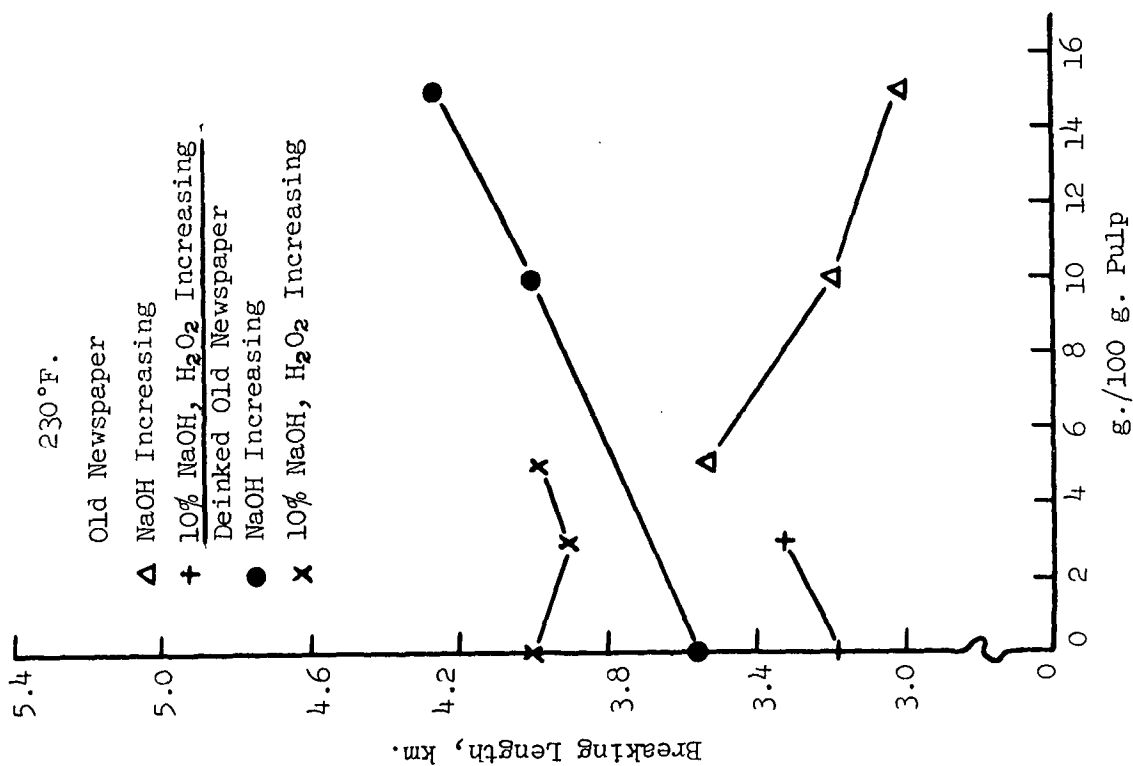


Figure 28. Breaking Length vs. Treatment

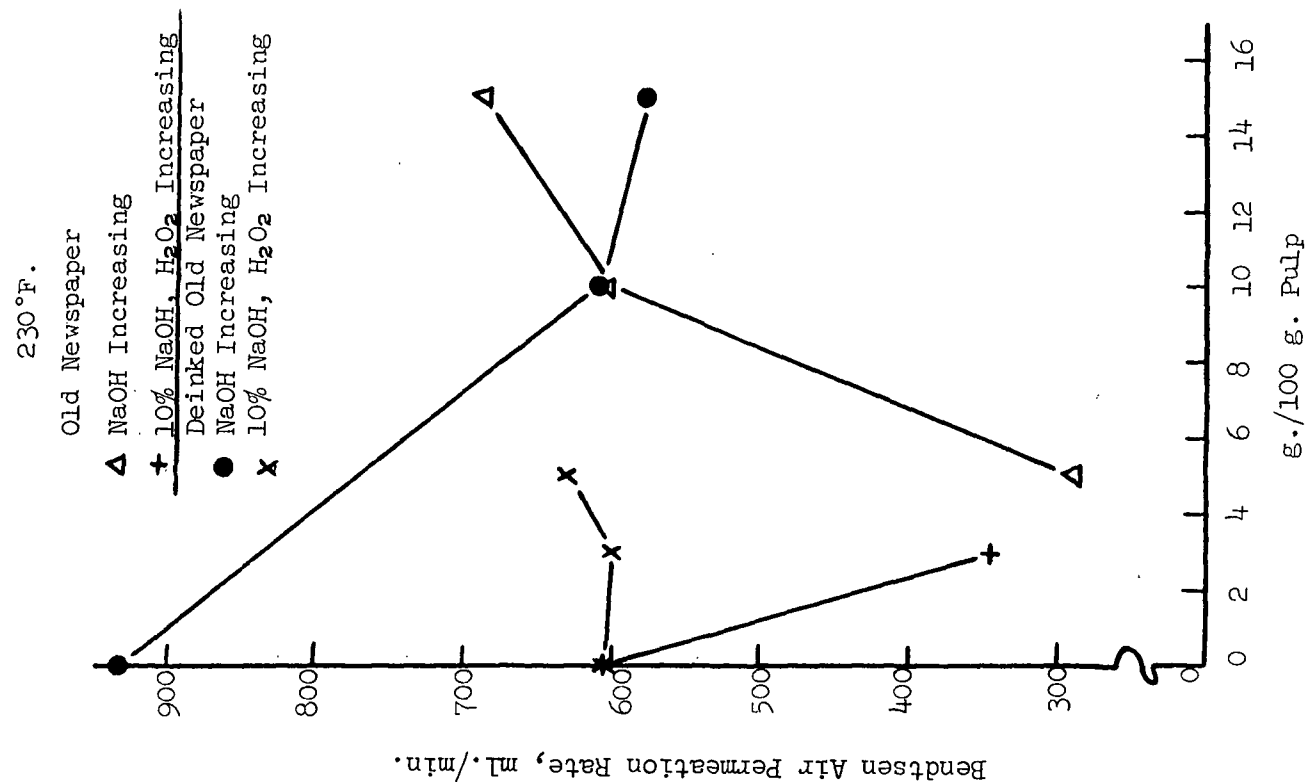


Figure 31. Porosity vs. Treatment

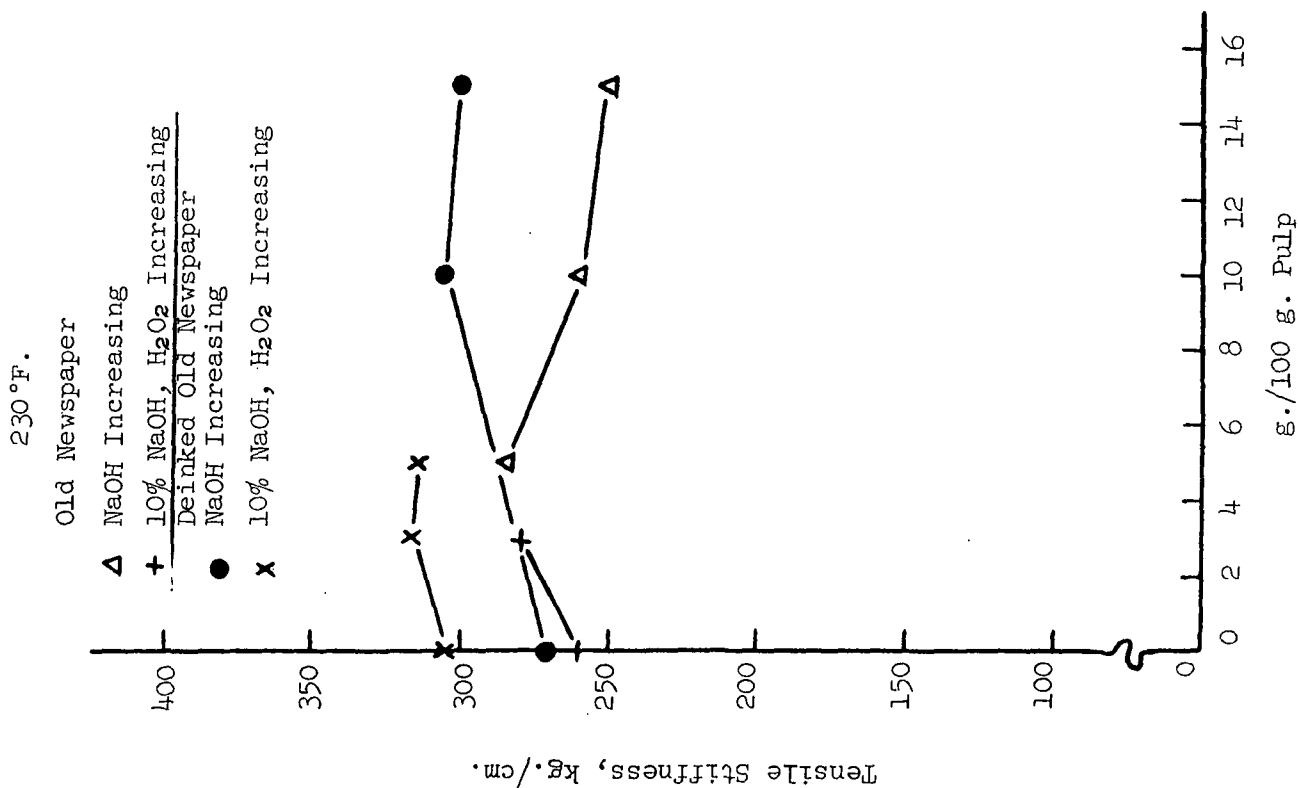


Figure 30. Tensile Stiffness vs. Treatment

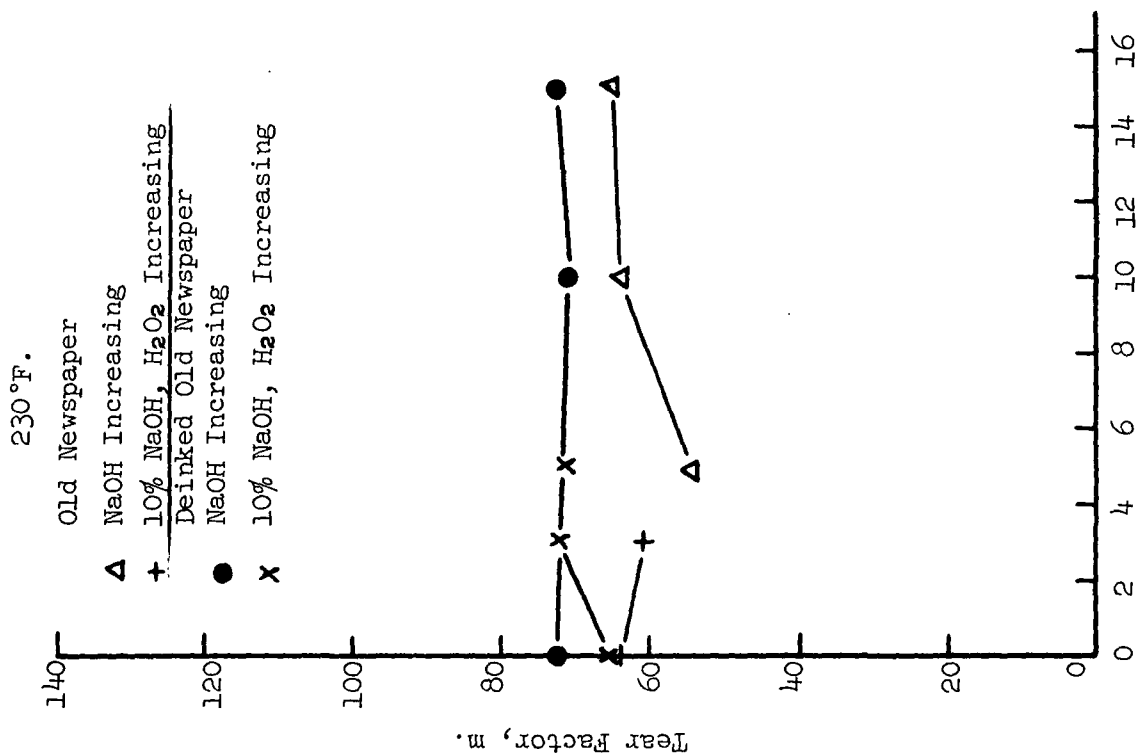


Figure 33. Tear vs. Treatment

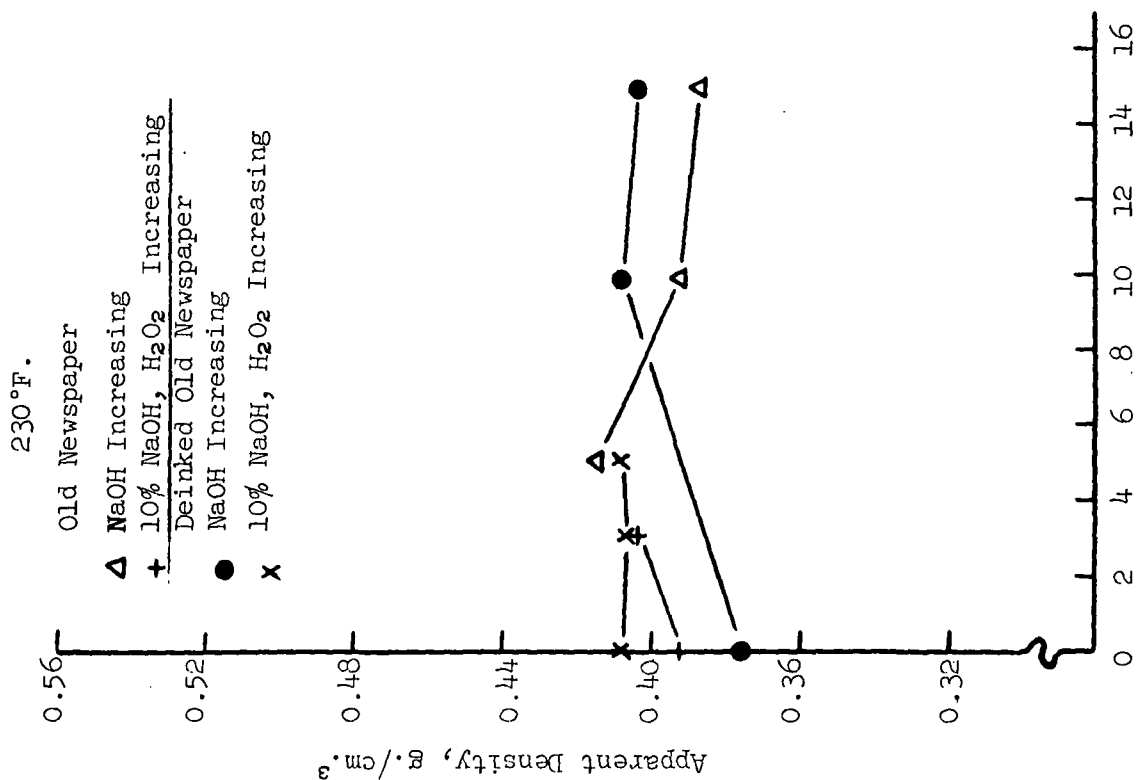


Figure 32. Density vs. Treatment

The tensile energy absorption values (Fig. 29) are changed by the caustic in the same manner as the tensile strength is changed but peroxide appears to have no effect upon either pulp. Tensile stiffness (Fig. 30) is not affected greatly by NaOH for either pulp but the deinked pulp values are raised and the nondeinked results are lowered. Peroxide improves the tensile stiffness of the nondeinked pulp but not that of the deinked form of the reclaimed fibers.

The air permeation rates are changed significantly by the caustic treatments (Fig. 31). That of the deinked pulp is lowered and that of the unpurified pulp is increased with greater amounts of NaOH. Peroxide has no effect on the deinked handsheet porosity while such treatment made the nondeinked handsheets less porous. The apparent density is relatively unchanged but conditions giving higher density also give higher tensile for both pulps (Fig. 32). The tear factors of the handsheets (Fig. 33) are not changed significantly by the treatments given either pulp.

The deinked newsprint furnish responds to the alkali and peroxide in about the same way (but not as much) as the aspen stone groundwood examined earlier in this report, while the nondeinked pulp shows performance patterns suggesting that debonding effects are produced by the caustic. This is a possibility. The mineral oil vehicle of the ink has not been washed out and could become better dispersed as the caustic concentration increases and then become redeposited more uniformly on the pulp surfaces during cooling.

#### DETERMINATION OF YIELD AND RESIDUAL CHEMICALS

There are four components in the treated pulps suspensions which are of interest in terms of their mass or concentration. They are the treated pulp itself, material extracted from the pulp, and unconsumed sodium hydroxide and

hydrogen peroxide. The amounts of these materials have been determined in respect to the amount of raw material added to the system. Aqueous phase concentrations can be obtained from the data given in Tables VII to X.

### Pulp Yield

This topic is the most critical in regard to the potential commercial acceptance of the jet/alkali process since yield losses tend to increase the cost of treated pulp rather quickly. The yield of treated pulp was determined gravimetrically from the oven-dry weight of duplicate samples of the neutralized, treated pulp suspension and of the filtrate, corrected for the salt content. The Appendix contains a detailed description of this procedure.

The yield data from Tables VII to X are plotted as functions of the processing conditions in Fig. 34 to 37. In general, the yields range from 98 to 93% for all conditions. The yields tend to decrease as the NaOH concentration increases for those pulps not having been treated with caustic before entering the jet/alkali process. Both the aspen chemirefiner pulp and the deinked news have been in alkaline systems during their preparation. The yields of these two pulps are affected to a lesser extent by the alkali concentration and range between 96 and 98%.

Bleaching reduces the pulp yield by 1% (chemirefiner, commercial softwood, deinked news) to 2% (aspen stone, nondeinked news) with almost all of the loss occurring between 0 and 1% peroxide. Raising the processing temperature of the bleaching system containing 10% NaOH and 3%  $H_2O_2$  has little effect upon the pulp yield except for the highest temperature (290°F.) used with the fluff-dried commercial softwood groundwood. In that instance, the yield dropped from 95 to 92% and corresponds with the greatest gain in tensile strength for that pulp.

TABLE VII  
ALFEN STONE GROUNDWOOD SUSPENSIONS

Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature, °F.	pH Pulp Slurry Before Cook	pH Pulp Slurry After Cook	Total Solids, g./100 g. slurry	Soluble Solids, g./100 g. slurry	Yield, %	Free NaOH, meq./100 ml. mg./g. solids	Combined NaOH, meq./100 ml. mg./g. solids	Total NaOH, meq./g. solids	% added	meq./100 ml.	Residual H <sub>2</sub> O <sub>2</sub> , mg./g. solids	% left
85	0	0	230	7.9	7.6	1.6520	0.0351	97.9	--	0.029	0.70	--	--	--	--
86	5	0	230	12.4	11.2	1.6398	0.1723	96.0	0.37	9.00	--	--	--	--	--
87	10	0	230	12.6	12.1	1.6403	0.2690	95.8	1.88	48.58	1.73	96.8	<0.002	<0.034	--
88	15	0	230	12.8	12.5	1.6857	0.3794	94.5	3.66	84.58	1.72	97.9	--	--	--
89	10	1	230	13.0	12.2	1.6884	0.2966	94.5	1.81	42.89	1.89	96.4	0.17	1.67	18.4
90	10	3	230	12.5	12.0	1.5477	0.2833	93.6	1.56	40.31	1.84	96.6	0.97	10.64	39.0
95	10	5	230	12.6	11.9	1.5864	0.2767	94.6	1.62	40.86	1.99	100.1	2.20	23.58	51.9
96	10	7	230	12.3	11.5	1.5892	0.2894	93.7	1.64	41.41	1.96	99.7	3.56	36.09	59.8
91	10	3	260	12.6	12.0	1.5646	0.2801	94.1	1.65	42.17	1.78	96.5	1.04	11.30	41.4
92	10	3	290	12.6	12.0	1.5543	0.2878	93.4	1.64	42.21	1.82	98.0	1.02	11.11	40.8
93	15	3	260	12.8	12.6	1.6425	0.3850	93.3	3.30	80.39	1.98	98.6	0.93	9.61	36.8
94	15	3	290	12.8	12.5	1.6705	0.3879	93.6	3.36	80.48	1.88	96.2	0.88	8.32	34.2
129 <sup>b</sup>	10	0	230	12.7	12.3	1.5513	0.2654	95.0	1.96	49.84	1.48	96.8	--	--	--
130 <sup>b</sup>	10	0	18	12.7	--	2.0054	0.2968	97.6	3.34	66.63	1.17	98.9	--	--	--
131	0	0	18	7.8	--	2.2696	0.0306	98.7	--	0.058	1.02	--	--	--	--

<sup>a</sup>Sum of free and combined NaOH over amount added.<sup>b</sup>Same pulp suspension; one part cooked, one part held at room temperature.

TABLE VIII  
ASPER CHEMREFINER GROUNDWOOD SUSPENSIONS

Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature, °F.	pH Pulp Slurry Before Cook	pH Pulp Slurry After Cook	Total Solids, g./100 g. slurry	Soluble Solids, g./100 g. slurry	Yield, %	Free NaOH meq./100 ml. mg./g. solids	Combined NaOH meq./100 ml. mg./g. solids	Total NaOH meq./100 ml. mg./g. solids	Total NaOH % added <sup>a</sup>	Residual H <sub>2</sub> O <sub>2</sub> mg./g. solids	% left
97	0	0	230	9.1	8.4	1.1554	0.040	96.5	--	0.063	2.36	2.36	<0.304	<0.06
99	5	0	230	12.5	12.1	1.6235	0.150	97.4	1.060	0.635	15.65	14.77	<0.0052	0.05
100	10	0	230	12.8	12.6	1.4772	0.235	96.4	2.600	0.575	15.57	35.37	0.004	0.07
98	15	0	230	13.0	12.8	1.5612	0.334	96.2	4.390	0.680	17.20	128.27	0.019 <sup>b</sup>	0.21
101	10	1	230	12.8	12.5	1.6942	0.288	95.1	2.770	0.905	21.37	86.78	0.222	2.23
102	10	3	230	12.7	12.5	1.4393	0.242	95.3	2.160	0.760	21.13	31.13	1.10	13.02
103	10	5	230	12.5	12.3	1.7218	0.295	95.0	2.555	1.075	24.97	84.32	2.24	48.7
104	10	7	230	12.5	12.1	1.7035	0.288	95.2	2.640	1.160	27.23	89.20	3.48	54.6
105	10	3	260	12.7	12.5	1.5905	0.275	94.7	2.515	0.855	21.50	84.73	1.18	46.4
106	10	3	290	12.7	12.5	1.4117	0.235	95.5	2.065	0.815	23.09	81.59	1.03	45.4
106	10	3	Raw slurry	12.7	--	2.1080	0.351	95.5	4.020	0.450	8.54	84.82	1.31	38.7

<sup>a</sup> Sum of free and combined NaOH over amount added.

<sup>b</sup> Tap water = 0.030 meq./100 ml. (probably chlorine).



TABLE IX  
SOFTWOOD MARKET GROUNDWOOD SUSPENSIONS

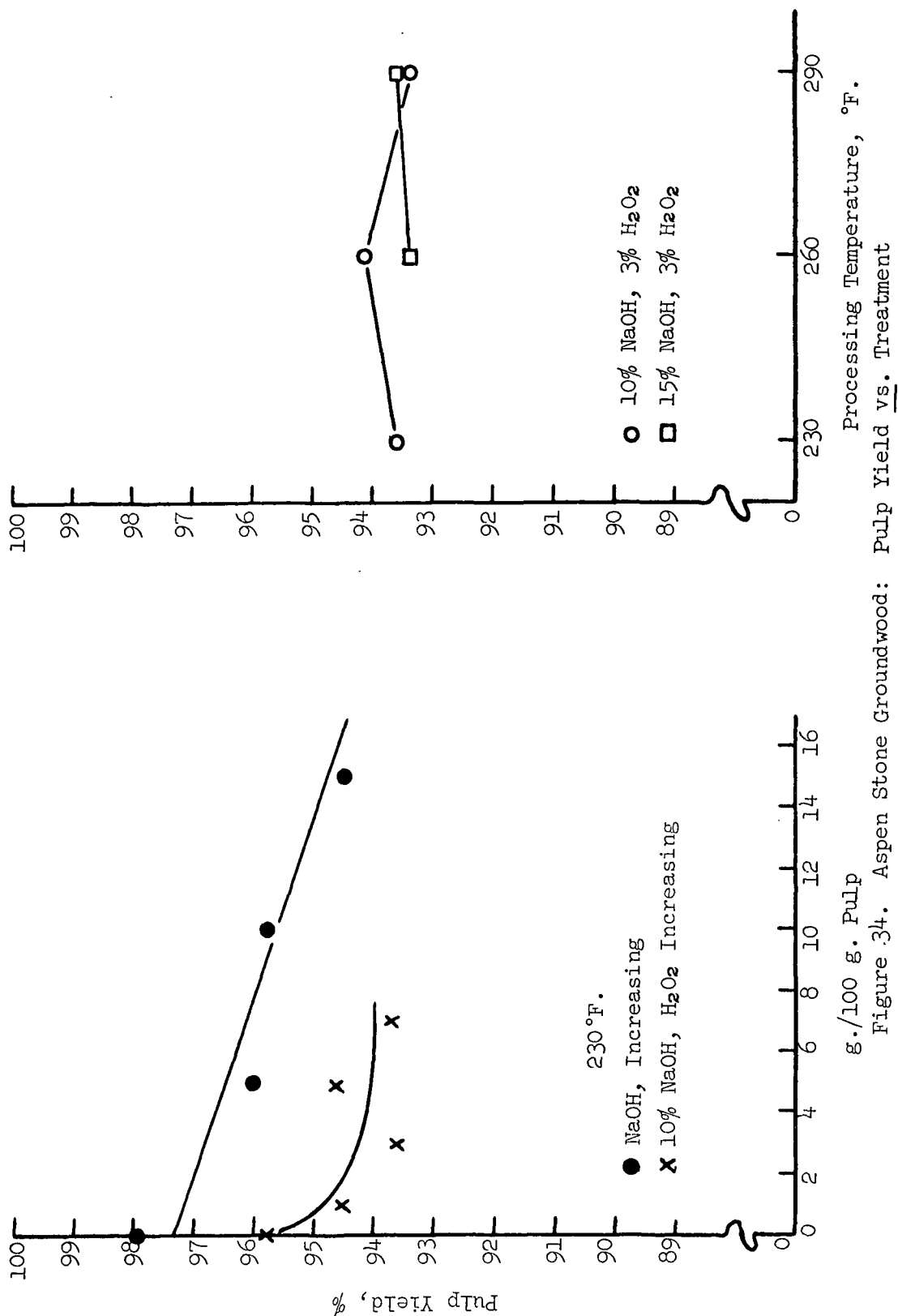
Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature, °F.	SR Pulp Slurry Before Cook	Yield, %	Total Solids, g./100 g. slurry	Soluble Solids, g./100 g. slurry	Yield, %	Free NaOH, meq./100 ml. slurry	Combined NaOH, meq./100 ml. slurry	Total NaOH, meq./100 ml. slurry	Residual K <sub>2</sub> O, meq./g. solids	% left
108	0	0	230	8.2	7.6	1.7117	0.0409	97.6	0.000	0.064	1.52	0.0152 <sup>b</sup>	--
109	5	0	230	12.5	12.2	1.6198	0.1496	97.4	0.880	0.525	12.96	34.69	72.3
110	10	0	230	12.8	12.6	1.7004	0.2795	95.8	2.890	0.640	15.06	82.82	91.1
111	15	0	230	13.0	12.8	1.7772	0.3868	95.4	4.700	0.735	16.54	122.45	93.9
112	10	1	230	12.8	12.6	1.8229	0.3060	95.4	2.680	0.985	21.61	80.42	83.5
113	10	3	230	12.6	12.5	1.5918	0.2268	94.7	2.130	1.050	26.38	79.91	87.9
114	10	5	230	12.5	12.5	1.7696	0.3034	95.0	2.125	1.300	29.38	77.41	35.2
115	10	7	230	12.4	12.3	1.7949	0.3080	94.9	1.945	1.375	30.64	73.99	91.4
116	10	3	260	12.7	12.5	1.7477	0.2944	95.3	2.365	1.185	27.12	81.24	59.4
117	10	3	290	12.7	12.6	1.7484	0.3400	96.3	2.590	1.240	28.37	87.64	96.4

<sup>a</sup> Sum of free and combined NaOH over amount added.<sup>b</sup> 0.0430 meq./100 ml. in tap water.<sup>c</sup> 0.0210 meq./100 ml. in tap water.<sup>d</sup> 0.0154 meq./100 ml. in tap water.<sup>e</sup> 0.0080 meq./100 ml. in tap water.

TABLE X  
RECLAIMED NEWSPAPER SUSPENSIONS

Ref. No.	NaOH Added, g./100 g. pulp	H <sub>2</sub> O <sub>2</sub> Added, g./100 g. pulp	Processing Temperature, °F.	pH Pulp Slurry		Total Solids, g./100 g. slurry	Soluble Solids, g./100 g. slurry	Yield, %	Free NaOH		Combined NaOH		Total NaOH mg./g. solids % added <sup>a</sup>	Residual H <sub>2</sub> O <sub>2</sub>	
				Before Cook	After Cook				meq./100 ml. mg./g. solids	meq./100 ml. mg./g. solids	meq./100 ml. mg./g. solids	% left <sup>c</sup>			
Nondeinked															
119	5	0	230	12.5	12.2	1.7321	0.1584	97.5	1.070	0.590	13.62	38.33	81.0	<0.0002	--
120	10	0	230	12.8	12.5	1.5659	0.2364	96.6	2.530	0.515	13.16	77.79	85.6	0.0070 <sup>b</sup>	--
121	15	0	230	13.0	12.8	1.7202	0.3569	96.6	4.530	0.630	14.65	120.99	92.0	0.0110	0.109
122	10	3	230	12.7	12.5	1.4790	0.2373	96.2	2.090	0.925	25.02	81.54	89.7	0.448 <sup>c</sup>	19.7
Deinked															
127	0	0	230	8.7	8.7	1.5046	0.0330	97.8	0.000	0.067	1.79	1.79	--	0.0080 <sup>d</sup>	--
123	10	0	230	12.8	12.6	1.6197	0.2277	98.5	2.975	0.350	8.59	81.61	89.8	0.0070	0.073
124	15	0	230	13.0	12.8	1.4699	0.3100	96.6	4.165	0.290	7.79	119.61	91.7	0.0120 <sup>e</sup>	--
125	10	3	230	12.6	12.5	1.5139	0.2285	97.3	2.535	0.550	14.53	81.51	89.7	0.502	5.64
126	10	5	230	12.5	12.2	1.4117	0.1996	98.4	2.360	0.460	12.92	79.79	87.8	1.424	17.15
		Tap water	--	--	--	--	--	--	0.0272	0.0658	--	--	--	--	--

<sup>a</sup> Sum of free and combined NaOH over amount added.  
<sup>b</sup> 0.0120 meq./100 ml. in tap water (Cl<sub>2</sub>).  
<sup>c</sup> 0.0140 meq./100 ml. in tap water.  
<sup>d</sup> 0.0222 meq./100 ml. in tap water.  
<sup>e</sup> 0.0196 meq./100 ml. in tap water.



g./100 g. Pulp

Figure 34. Aspen Stone Groundwood: Pulp Yield vs. Treatment

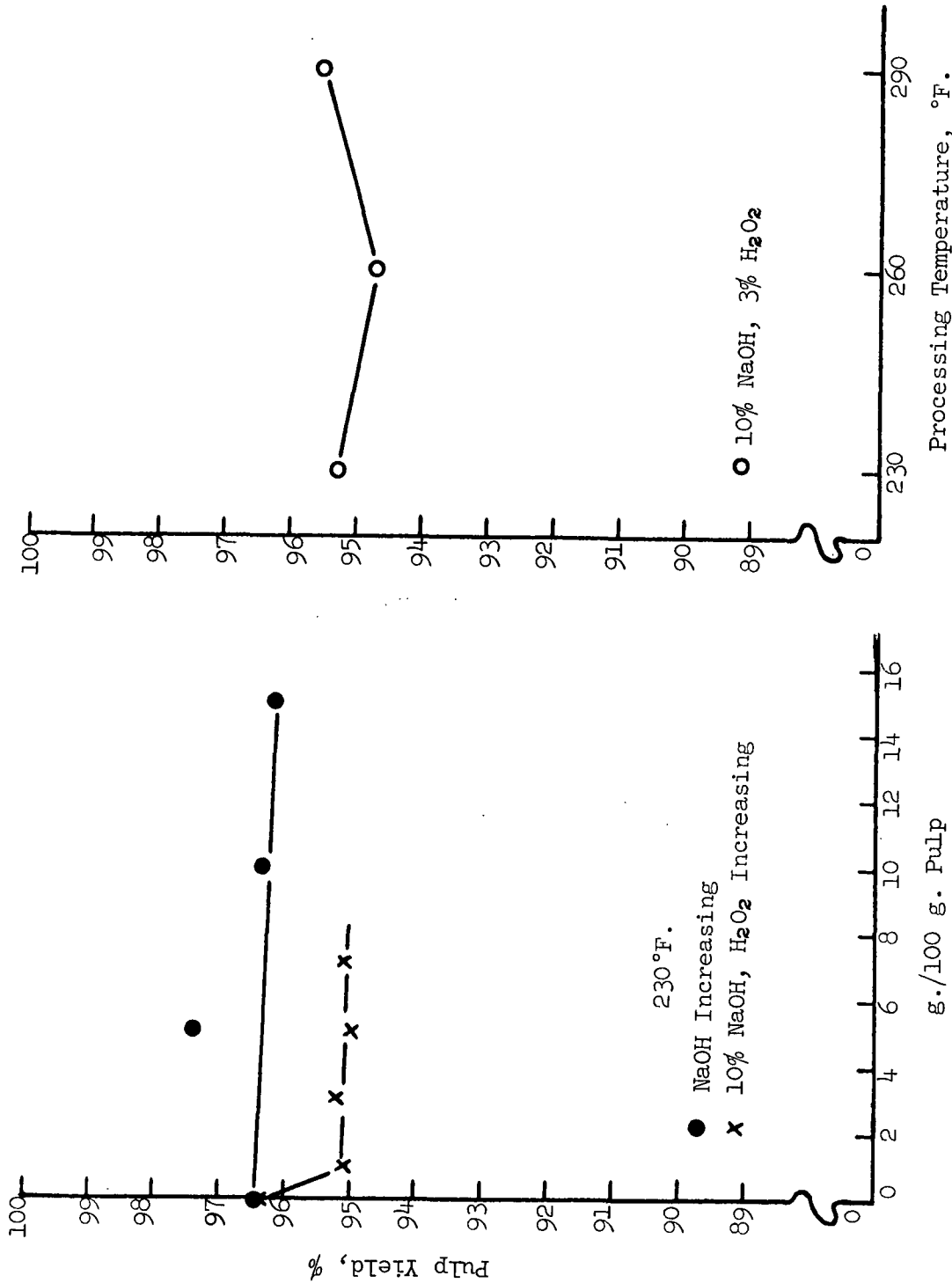


Figure 35. Aspen Chemirefiner Groundwood: Pulp Yield vs. Treatment

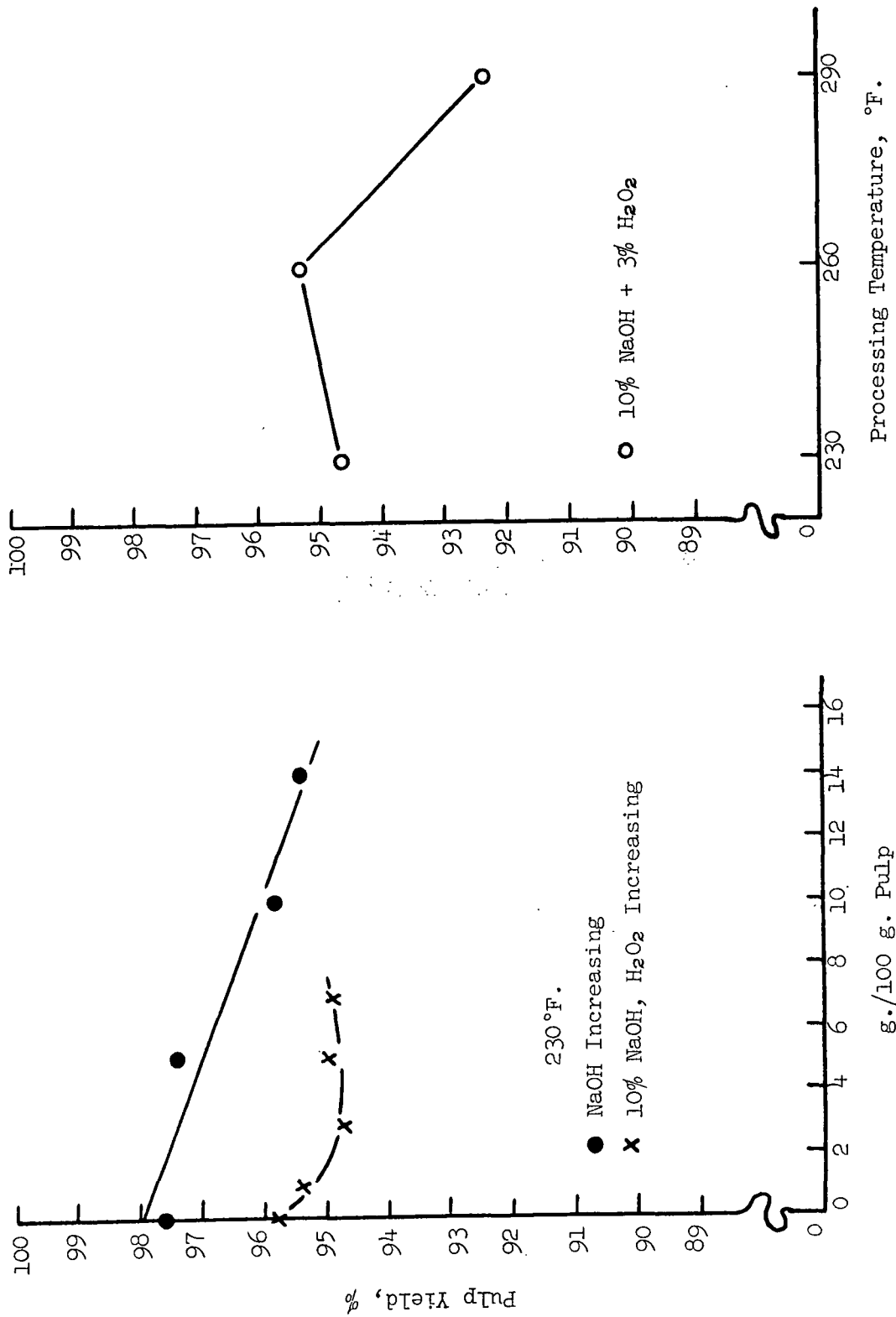


Figure 36. Softwood Market Groundwood: Pulp Yield vs. Treatment

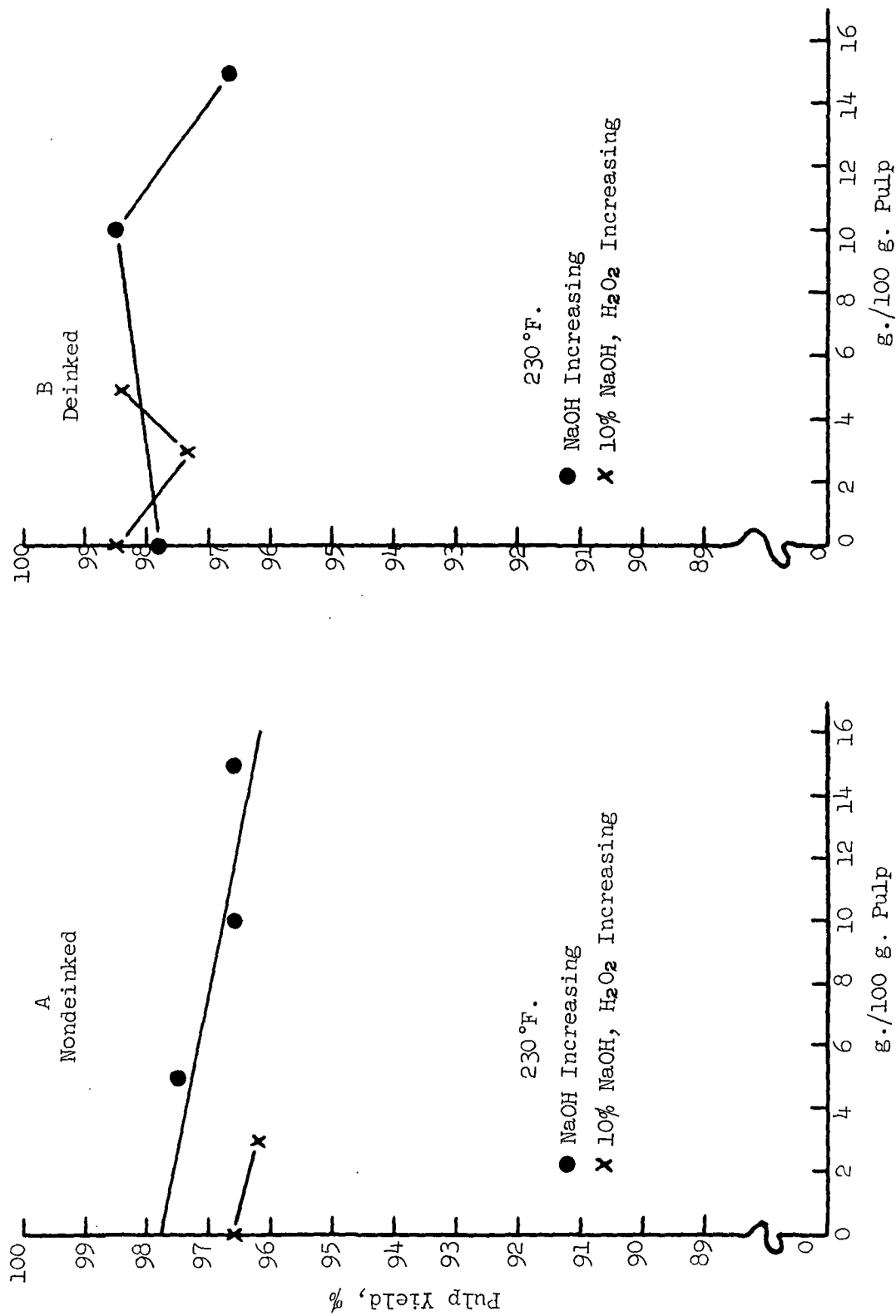


Figure 37. Reclaimed Newspapers: Pulp Yield vs. Treatment

The yields of raw, untreated pulp were 98.7% for the aspen stone groundwood (Table VII) and 97.9% for pulp cooked at 230°F. without caustic or peroxide (Table I).

#### Estimate of Cost Reduction Potential

The pulp losses due to the jet/alkali are not excessive. Assuming a yield of 95%, the cost of treated pulp is raised only 5.3% due to this loss of usable material.

At essentially unchanged tensile energy absorption values, 80% treated aspen stone or chemirefiner pulp and 20% kraft pulp blends can replace 50% untreated groundwood and 50% kraft furnishes (see Fig. 14 and 15). Both groundwoods would be treated with 10% NaOH at 230°F. Assuming the bleached kraft pulp costs twice as much as the untreated groundwoods and yields of 95% are obtained, then a ton of the 50/50 furnish would cost 1.50, and a ton of the 80/20 furnish 1.24 times the cost of a ton of untreated groundwood — a 19% reduction in furnish cost. No allowance has been made for processing costs nor a value assigned to the higher tensile strength which would be obtained by this substitution. However, the consumption of processing chemicals is not excessive, as shown in the next two sections of this report, and detracts little from the attractiveness of the cost-reducing potential.

#### Hydrogen Peroxide

The amount of hydrogen peroxide unconsumed by the treatments has been discussed to some extent earlier in the report in regard to the brightness of the virgin groundwood pulps. These data are plotted in Fig. 4. From 20 to 60% of the 1 to 7% peroxide added remains after 230°F. processing of the aspen stone groundwood and aspen chemirefiner pulps. The percent unreacted increases with the amount added indicating that the reaction conditions were not efficient

in terms of bleaching but considerable amounts of peroxide are available for reuse.

The maximum amount of unused peroxide was obtained from the treatment of the aspen stone groundwood at the 7% level. This was 3.58 milliequivalents per 100 ml. and was reduced to that level by dilution in the cooker as well as consumption of 40% of the amount added. This is equivalent to the aqueous concentration which would be obtained by adding 2.5% peroxide on the weight of the pulp at a consistency of 2%. Thus, the unused bleach should be available for recycling in the process.

There are a number of options in regard to recovering brightness lost by alkaline browning and to bleaching the treated pulp. These include a separate bleaching step and simultaneous treatments to bleach and to improve bonding. Further work is needed in regard to the latter possibility and should include evaluation of different bleaching systems as well as steps to improve peroxide bleaching.

#### Sodium Hydroxide

Two inflections are found in the electrometric titration curves of filtrates obtained from samples taken before neutralizing the processed pulp. The first inflection is consistent with the titration of a strong base with strong acid (0.1N HCl) and the second with the titration of the conjugate base of a weak acid, such as most organic acids. The first inflection is presumed to be related to the amount of free, uncombined sodium hydroxide and the difference in HCl milliequivalents between the second and the first inflection is presumed to be a measure of the amount of sodium hydroxide which has combined with wood acids either initially present in the pulp or produced by the treatment. The free NaOH probably is available for reuse by recycling the process



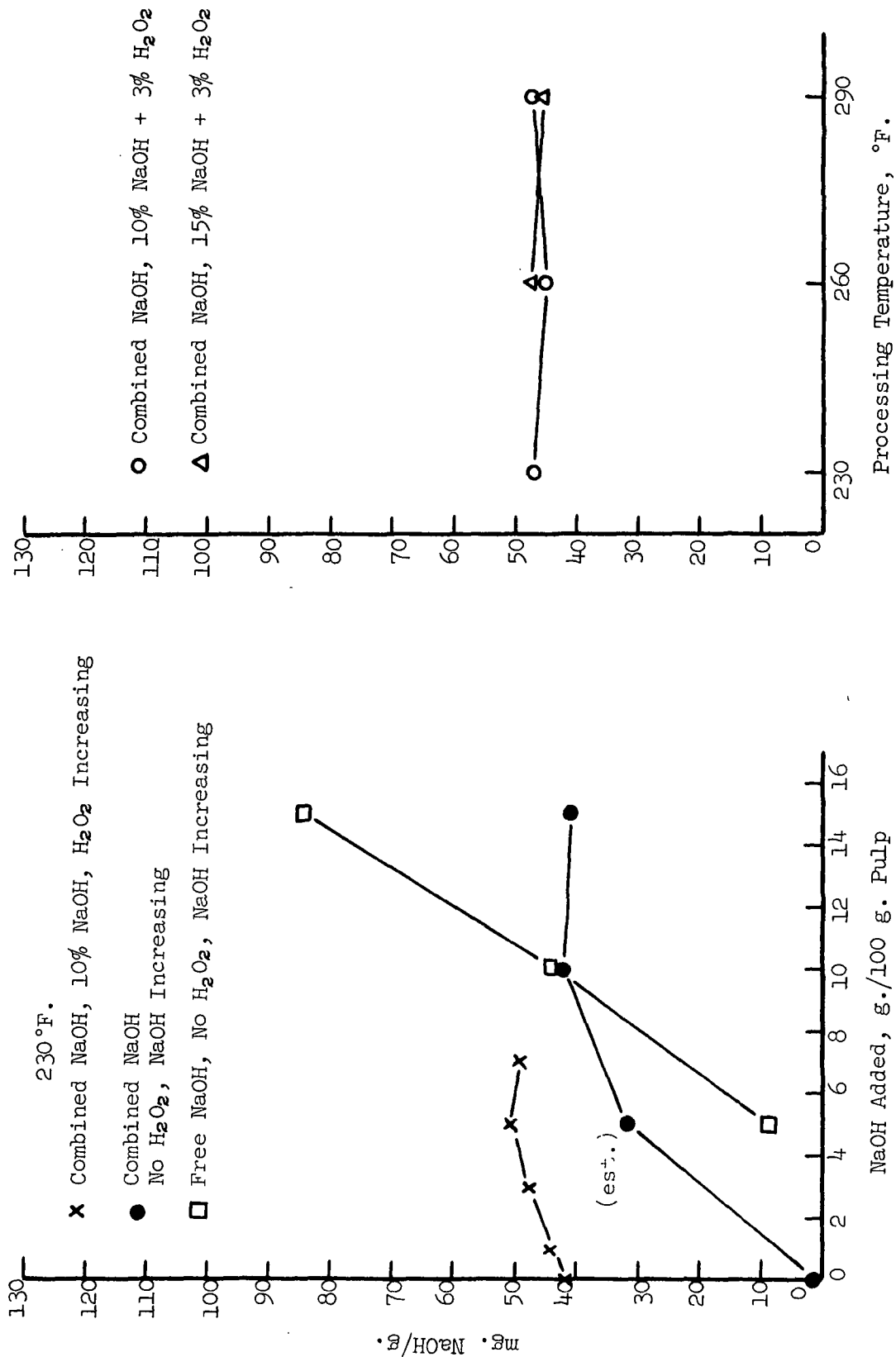
liquors while the combined NaOH must be reclaimed or discarded in an acceptable manner.

The concentration of free and combined NaOH has been expressed as milliequivalents per 100-ml. filtrate, in Tables VII to X, and then calculated as milligrams per gram total solids of the neutralized pulp suspension. This calculation is an estimate of the milligrams NaOH per gram of raw pulp.

The combined NaOH data also represent to a degree the amount of acidic material extracted from the pulp. The combining weights of the organic acidic material need to be known to state the relative weights of acidic and neutral extracted materials.

In Fig. 38 to 41, the amount of combined sodium hydroxide increases very little with increasing amounts of caustic added to the pulp. The pulp having the highest level, aspen stone groundwood in Fig. 38, reaches a plateau at 40 mg./g. at 10 and 15% NaOH. This, along with the trends shown in Fig. 39 to 41, suggests that the amount of NaOH consumed is a function of the pulp being treated and is not used up by acidic material produced during the exposure to alkali. Increasing dosages of peroxide are accompanied by increasing levels of combined NaOH. This indicates the oxidizing agent is producing acidic products to some extent. The fact that the amount of unreacted peroxide is increasing at the same time the level of combined NaOH is relatively stable shows there is a limit to the amount of acidic material produced by the peroxide.

The processing temperature has little, or no effect upon the consumption of sodium hydroxide for the treatments with 3%  $H_2O_2$  and 10% NaOH. Increasing the caustic level to 15% with 3%  $H_2O_2$  has no effect upon the alkali consumption at 260 or 290°F. with aspen stone groundwood.



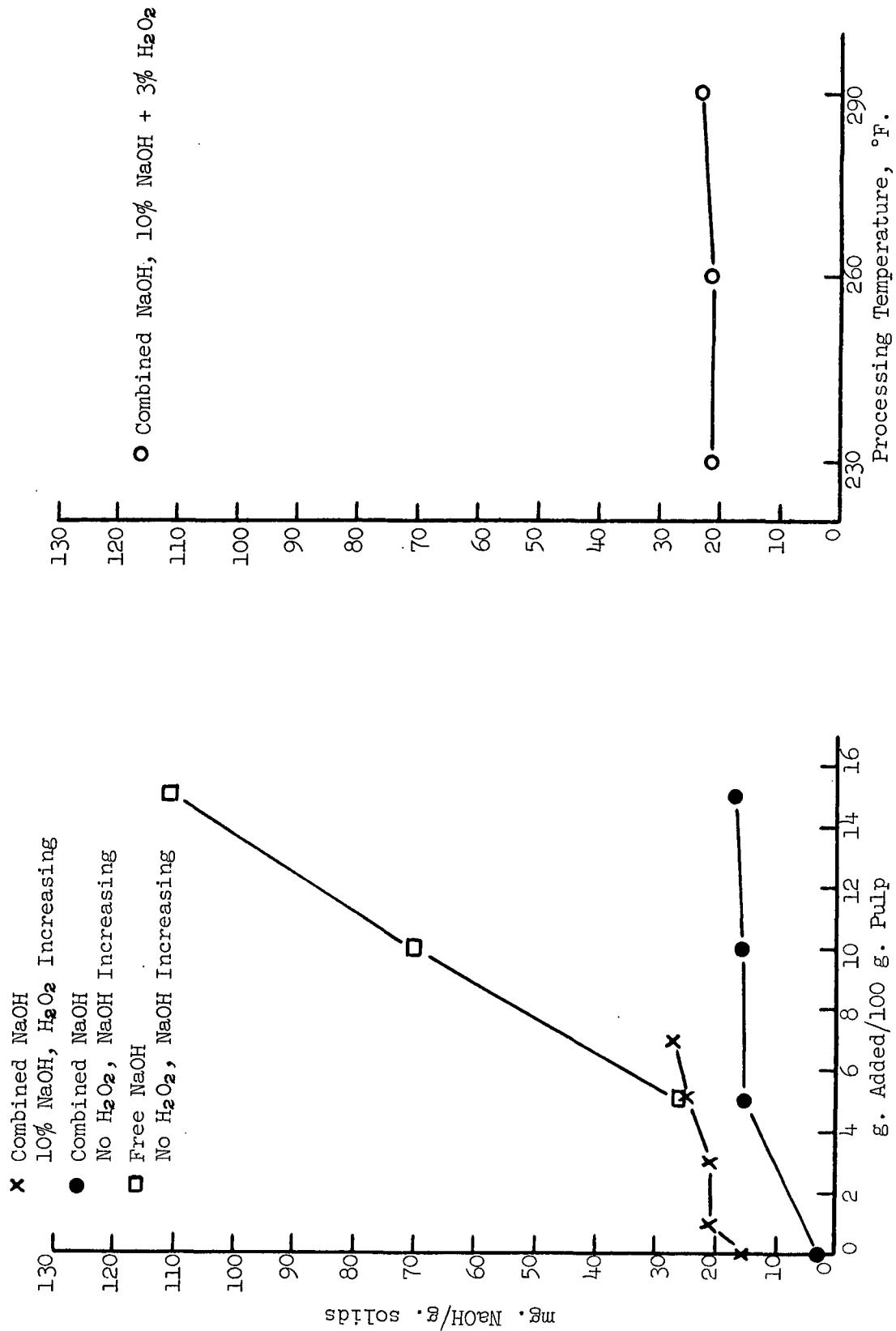


Figure 39. Aspen Chemirefiner Groundwood: Free and Combined NaOH vs. Treatment

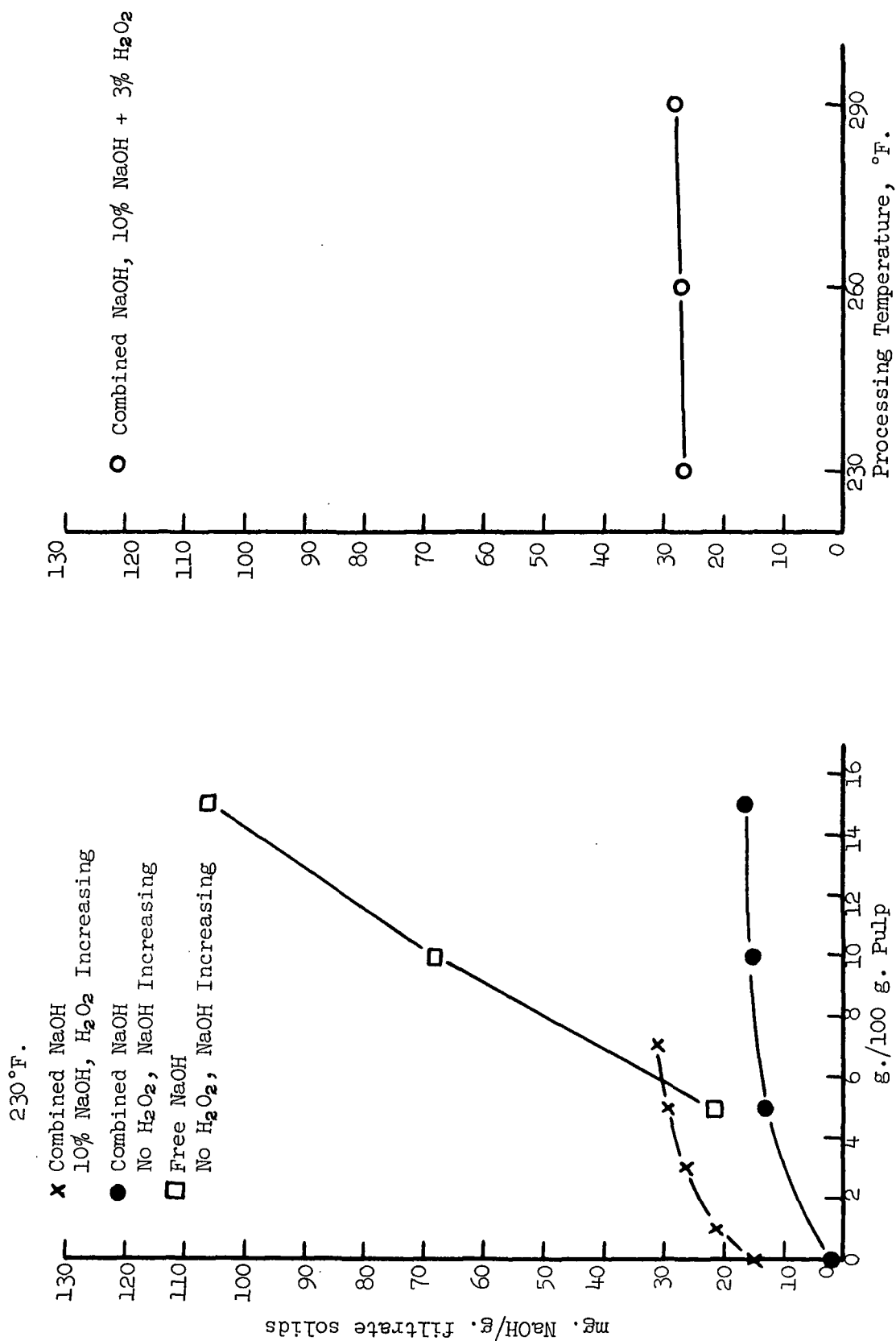


Figure 40. Softwood Market Groundwood: Free and Combined NaOH vs. Treatment

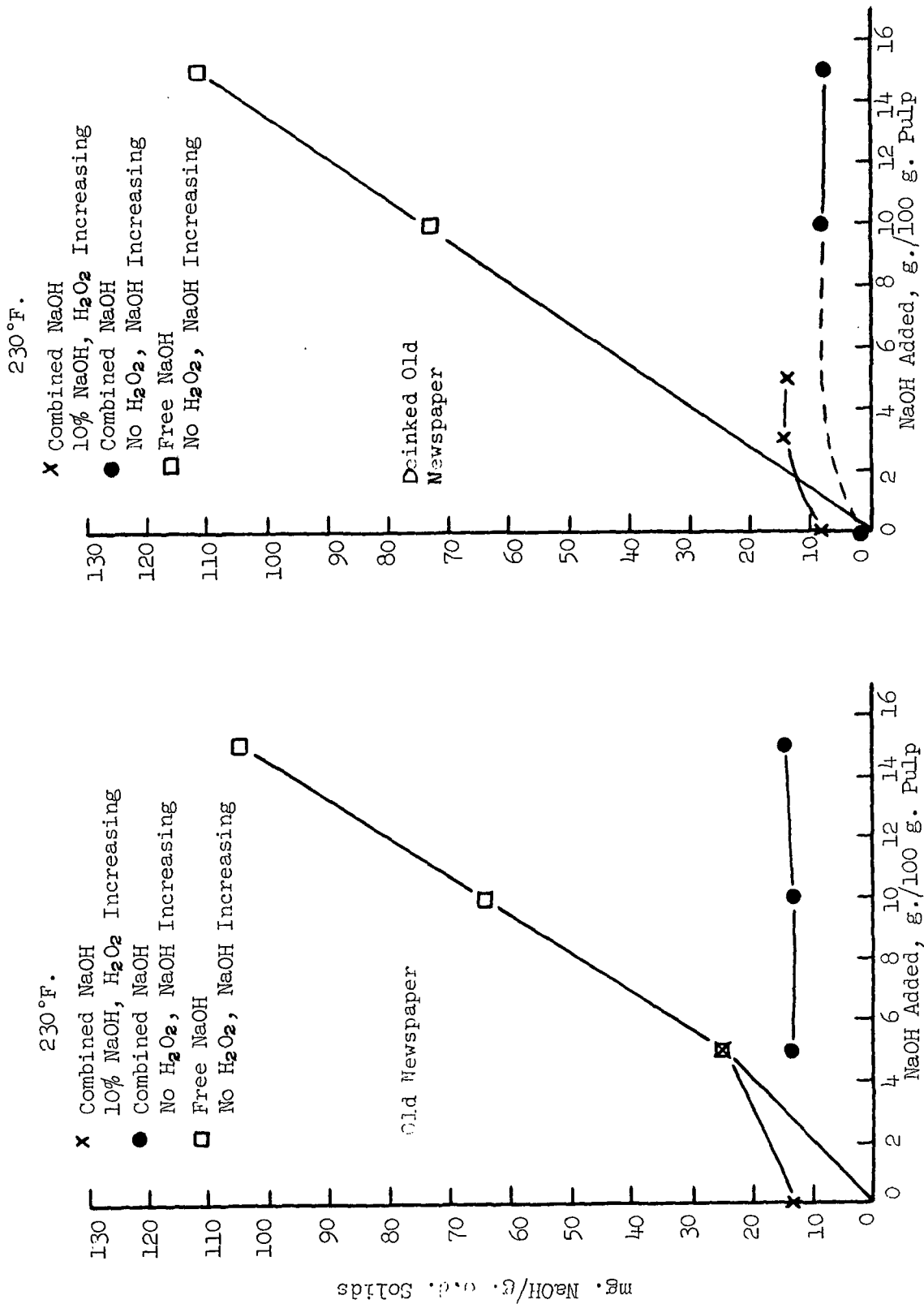


Figure 41. Reclaimed Newspapers: Free and Combined NaOH vs. Treatment

The concentration of free NaOH is reduced by dilution in the jet cooker and by the acidic material. Depending upon the amount added initially, the free NaOH concentrations range from 0.4 to a maximum of 4.7 milliequivalents per 100 ml. (see Tables VII to X). On a weight basis, this is equivalent to 0.016 to 0.19 gram per 100 ml. The lowest value is from the treatment of the aspen stone groundwood with 5% NaOH. Since this pulp produces the greatest amount of combined NaOH, it is less likely recoverable amounts of NaOH would be obtained from treatments of this pulp with lower amounts of caustic. The initial concentrations of sodium hydroxide in the 2% consistency pulp were about 0.1 to 0.3 g. per 100 ml.

It is expected that the amount of NaOH required for a given level of bonding will be a function of both the pulp consistency and the aqueous phase alkali concentration. Thus, the amount of caustic based on the pulp should be reduced at higher consistencies. If this should be the case, then a smaller percentage of the caustic added would be recovered as free alkali. Doubling consistency would halve the amount of free NaOH needed to produce the same concentration of free NaOH in the aqueous phase, and should double the amount of combined NaOH in the process liquor.

#### COMPARISON OF BONDING STRENGTH

The breaking length values for all five pulps are plotted in Fig. 42 as functions of the alkali concentration for treatments at 230°F. The two aspen pulps produce the highest tensile strength levels and show the greatest improvement with increasing amounts of sodium hydroxide. The softwood pulps, represented by the fluff-dried market pulp and the deinked newsprint, also show improved tensile strength with rising NaOH concentrations. The tensile strength of the

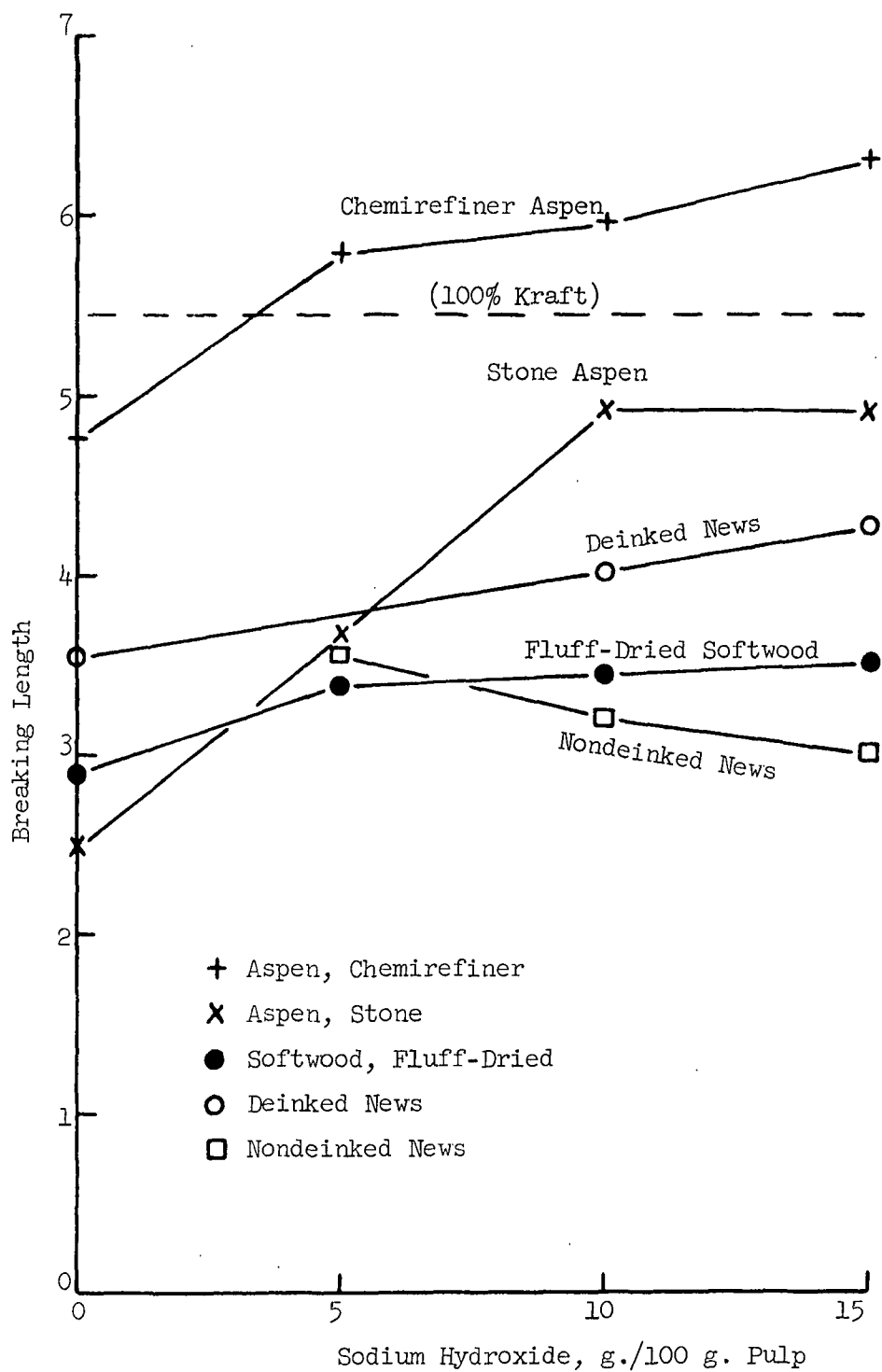


Figure 42. Breaking Length vs. NaOH Concentrations at 230°F. Summary of Pulps

nondeinked newsprint is reduced by adding sodium hydroxide beyond the 5% level. Part of the poorer response is thought possibly to be due to debonding effects of the newspaper ink. Since the tensile strength of the nondeinked pulp, treated with 5% NaOH, is almost identical to the values for the aspen stone groundwood and the market softwood pulp treated in the same way, it is likely that the reclaimed pulp also has benefited from the treatment. The jet/alkali treatment has improved the tensile strength of the softwood pulp by 20% and of the hardwood pulp by 40% over the values obtained from the samples heated without caustic. In addition to this, the tensile strength of the softwood market pulp has been raised 40% just by jet-cooking the neutral slurry. Consequently, it is almost certain that the reclaimed softwood newsprint furnish would also be improved by these combined treatments.



## CONCLUSIONS AND RECOMMENDATIONS

## ASPEN PULPS

There is a high potential for substantial cost reductions for mixed furnishes by replacing part of the chemical pulp with jet/alkali-processed aspen chemirefiner and stone groundwood pulps. Tensile strength values for handsheets from 80/20 blends of treated groundwood and untreated kraft either attain 90% of the tensile strength of the all-kraft control handsheets (stone pulp) or exceed the tensile strength of the controls by as much as 40%. Tensile energy absorption values of the 80/20 blends are improved significantly while tearing resistance is unharmed. The yields of treated aspen pulps are high ranging from 93 to 98%.

Recommended Action

Continue development of the jet/alkali process for aspen groundwoods with the aim of early commercialization. Establish the relationships of processing temperature, alkali concentration, and pulp consistency with regard to bonding improvement and chemical consumption and reuse in order to guide selection of the optimum processing conditions for specific uses.

\*\*\*\*\*

Bleaching and bonding improvement can be combined in the jet/alkali process. With recycling of the bleach liquor, economically sound results are expected. Aspen stone groundwood treated at 230°F. with 10% NaOH had a pulp brightness of 48.9% which was raised to 73.3% by adding 7% hydrogen peroxide. After processing, 60% of the peroxide was available for reuse. Thus, 2.8 g. H<sub>2</sub>O<sub>2</sub> per 100 g. o.d. pulp raised the brightness of the pulp 24.4 points or 8.7 points per percent consumed. The bleaching effect was accomplished within 6 seconds in the jet cooker plus the 10-minute interval required to cool the

the pulp from about 195°F. to room temperature. The untreated starting material had a brightness of 63.1%.

#### Recommended Action

Include bleaching as part of the development of the jet/alkali process for groundwood not only with the view of correcting the brightness loss due to the sodium hydroxide treatment and of bleaching the groundwood pulp, but also with the possibility of extending the operation to bleaching other pulps in mind. The effectiveness of recycled reagents needs evaluation along with the value of the excess alkali from sodium peroxide in reducing the NaOH requirement. The possible beneficial effects of additives, such as sodium silicate, upon the bleaching reaction need to be balanced against possible effects upon bonding improvement. Consideration should be given to other bleaching reagents and to the effect of the rate of cooling the pulp after the treatment upon bonding, brightness, and reclamation of unused reagents.

#### OTHER HARDWOOD PULPS

Hardwood species in general are valued sources of groundwood pulps. However, no information is available which demonstrates that hardwoods as a class can be expected to respond to the jet/alkali treatments in the manner shown for the aspen chemirefiner and stone pulps.

#### Recommended Action

Carry out screening experiments with selected hardwood species groundwood pulps to evaluate the general applicability of the jet/alkali process.

## SOFTWOOD PULPS

Treatment of softwood groundwood by the jet/alkali process either is incapable of producing the outstanding improvements obtained with the aspen pulps or the softwood pulps require different processing conditions than the aspen pulps. The single example of this class of pulps examined this far, responded to increasing alkali like the hardwood pulps but to a lesser degree. However, unlike the hardwood pulps, the bonding strength of this northern softwood groundwood market pulp also improved with increasing amounts of peroxide and with increasing process temperatures. Thus, the more drastic the processing conditions the better the bonding enhancement. These clues suggest further bonding improvement may be possible by choosing conditions to accommodate differing characteristics of this class of groundwood pulps.

Recommended Action

Treat softwood groundwoods of well-defined species with increasing amounts of NaOH, extending into the range of concentrations used in alkaline pulping, at jet cooker processing temperatures significantly higher than 230°F., along with several levels of peroxide. Bonding improvement in mixed furnishes should be correlated with the treatment conditions. But, in addition, changes in fiber length distribution (7) and chemical composition of the treated pulps need to be related to changes in the processing conditions: not only for selected softwood pulps but also for aspen pulps to provide a rational basis for further changes in processing parameters.

## RECYCLED GROUNDWOOD PULPS

The reclaimed softwood groundwood pulp obtained from deinked old news papers responded to the jet/alkali processing like the virgin softwood groundwood and to a lesser extent than the aspen pulps. Therefore, improved processing procedures developed for softwood groundwoods in general should also benefit deinked, recycled, softwood groundwood pulps.

The nondeinked newspaper groundwood furnish produced handsheet tensile strength values with 5% NaOH like those obtained with the softwood groundwood and aspen stone groundwood treated with the same amount of caustic and tested in 80/20 groundwood/kraft blends. Further, the value predicted for the deinked pulp treated with 5% NaOH (based on the linear improvement as the caustic treatment increased from 0 to 10 to 15%) lies very near that of the value for the nondeinked pulp. Thus, it is highly probable that the lower tensile values for the handsheets made from the nondeinked pulp as the treated material was cooled down to room temperature.

### Recommended Action

Carry out confirmatory experiments with the deinked pulps to show that improved processing conditions developed for softwood pulps are also effective with the reclaimed pulp. For the nondeinked newspaper pulps, seek ways to avoid redeposition of the ink: possibly by differential sedimentation or by selection of emulsifying agents which are not also debonding agents.

#### ACKNOWLEDGMENTS

The assistance of Mr. Don Gilbert in treating the pulps and preparing the handsheets is greatly appreciated. Mr. J. Hankey ably performed the microscopic analyses of the fluff-dried groundwood and the deinked newsprint.

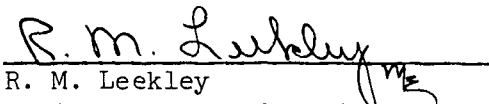
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## APPENDIX

### PULPS USED

#### BLEACHED WESTERN SOFTWOOD KRAFT

Rayonier WBS-W dry lap (2.3 kg.) was soaked overnight in tap water and refined to 700-ml. Schopper-Riegler freeness (S.-R.) in a "5-pound" Valley beater. A sample from the beater also gave a reading of 350 ml. with the Canadian Standard Freeness (C.S.) instrument. The refined pulp was dewatered by vacuum filtration on a Buchner funnel covered with a sheet of gum rubber. The filter pad was broken up mechanically for ease of handling. After blending, the pulp crumb (22.7% solids) was stored under refrigeration for at least two weeks before use.

When needed, portions of this pulp were redispersed in tap water at 2.5% consistency for 300 counts in the British disintegrator and then diluted to 2.0% consistency.

#### ASPEN STONE GROUNDWOOD

About 350 pounds of pulp at 4-6% consistency from the decker was donated by one of the cooperators. This pulp was dewatered (19.7% solids) and refrigerated until needed. This pulp is an unbleached form of the pulp used in Report One.

As needed, the pulp was resuspended in tap water at 2.5% consistency for 300 counts in a British disintegrator and then diluted to 2.0% consistency.

## ASPEN CHEMIREFINER GROUNDWOOD

This pulp was donated by another cooperator as partially dewatered stock. Vacuum filtration and pressing on a Buchner funnel covered with rubber sheeting raised the solids to 20.7%. The filter pads were fragmented mechanically, blended and stored under refrigeration.

As needed, the wet pulp was resuspended in tap water at 2.5% consistency for 300 counts in the British disintegrator and diluted to 2.0% consistency.

## SOFTWOOD GROUNDWOOD

A sample of commercial, fluff-dried groundwood was donated by one of the cooperators. This pulp had been on hand for several months and was identified as "South Nelson." Presumably this material was obtained from Acadia Pulp Co. in New Brunswick. Microscopic examination confirmed this sample contained 100% softwood species and that "the fiber furnish contains a fairly large amount of long pieces of fibrous material. The fines fraction is made up principally of "flour" (i.e., fine platelike material having a grainy appearance) and is relatively free of "mucus" (extremely fine particles which appear as fine dots, the presence of which causes a substantial densification of the sheet. Microscopic examination would indicate the probability that the sample is refiner rather than stone groundwood. A high freeness value (100+) would also indicate the probability of refiner rather than stone groundwood."

As needed, 100-gram portions of dry pulp were dispersed for 300 counts in a British disintegrator, soaked overnight and agitated for an additional 300 counts before being diluted to 2.0% consistency.

#### OLD NEWSPAPERS

Approximately equal proportions of back issues of the Appleton Post-Crescent and the Wall Street Journal were torn into small squares and dispersed 50.0 g. o.d. at a time, in 2000 ml. tap water for 300 counts in the British disintegrator. Two batches were combined and made up to 5000 ml. or about 2% consistency. This slurry was then treated and pumped through the jet cooker, cooled, neutralized to pH 5, and used directly to make handsheets after determining the consistency.

#### DEINKED NEWSPAPERS

Five batches of old newspapers were torn up and treated, 175 g. at a time, in 4 liters water containing 3.5 g. sodium silicate (2% of paper weight) 22 ml. 2N sodium hydroxide (1% NaOH) and 1.30 g. Igepal CO-630 (0.75% as is). The torn up papers were added slowly to the water in a large stainless steel Waring Blendor. A 15-watt Powerstatt was used to regulate the speed of the blendor at the maximum rate of stirring not producing splashing of the contents. The blendor was run for an additional 5-minute period after all the paper had been added.

The pulp was drained on the Noble and Wood sheet mold equipped with a 52 x 72 wire and then resuspended two times in 6 liters of tap water. Several smaller portions of the pulp were drained on an 8-inch sieve (No. 50 U.S. Standard Series) and washed on the sieve with a stream of hot tap water. All of the washed batches of pulp were blended into one suspension (1.74% consistency) and refrigerated until needed (about 5 days). About 71% of the dry newspaper is contained in this pulp. It was not blended with the bleached kraft pulp to make handsheets, but used directly from the treatment process.



Microscopic examination showed approximately 20% softwood unbleached sulfite (spruce, hemlock), 5% softwood bleached kraft (spruce, hemlock, jack pine), and 75% softwood groundwood containing (less than 5%) hardwood species.

#### PULP TREATMENTS

The treatment levels used in these studies were: 0, 5, 10, and 15 parts NaOH per 100 parts dry pulp, 0, 1, 3, 5, and 7 parts by weight  $H_2O_2$  per 100 parts dry pulp and processing temperature of 230, 260 or 290°F. (110, 127, and 143°C.). The combinations of these variables actually used are shown in the tables listing the pulps individually.

Five liters of pulp (100 g. o.d., 2% consistency) were treated with the desired amounts of 2.0N NaOH and 31.4% hydrogen peroxide, blended for about 5 minutes and processed in the jet cooker. About 3 liters of the cooker effluent was collected and cooled to room temperature within about 10 minutes. The suspension was sampled for determination of residual NaOH and  $H_2O_2$  and then neutralized with dilute hydrochloric acid to pH 5. At this point, the suspensions was sampled to determine the consistency (TAPPI Method T 240 su-67), Canadian Standard freeness, and yield.

#### PREPARATION OF MIXED FURNISHES

The 80/20 groundwood/kraft furnishes were prepared by blending part of the neutralized, treated groundwood suspension (32.0 o.d. pulp, volume based upon the consistency determination) with 400 ml. of a dispersion of the aged, refined bleached kraft pulp (8.0 g. o.d., from a 2% consistency suspension prepared daily).

Controls were prepared by blending the kraft pulp with untreated suspensions of the aspen stone and chemirefiner pulps and the softwood stone groundwood pulps. In addition to blends of 80/20 groundwood and kraft by weight, blends containing 50/50 proportions were prepared along with one suspension containing the kraft pulp by itself.

The treated groundwoods, it is noted, were used directly from the neutralized effluents from the jet cooker. There was no washing or screening after the cooker treatment and all of the salts and extractives are present in the aqueous phase. The only washing the treated pulps received was during handsheet formation.

#### HANDSHEET MAKING

The pulp suspensions were diluted to 0.5% consistency with tap water and adjusted to pH 5.0 with dilute sulfuric acid. The tap water in the sheet mold was also adjusted to pH 5.0 before 500-ml. aliquots of the furnish (2.5 g. pulp) were added to make 8-inch by 8-inch Nobel and Wood handsheets on a 100-mesh Monel wire. White water was not recirculated. The wet handsheets were couched onto blotters, pressed between blotters four sheets at a time for 5 minutes at 50 lb./in.<sup>2</sup> gage pressure and dried on the wire side blotter with the blotter against a drum containing steam at 3-5 lb./in.<sup>2</sup> gage pressure.

#### HANDSHEET TESTING PROCEDURES

The handsheets were equilibrated to 20% relative humidity at 70°F. and then to 50% R.H. at 72°F. before testing according to TAPPI Procedures. Brightness tests were made within 24 hours of preparation on unequilibrated paper.

## ANALYTICAL METHODS

Residual NaOH

Samples of the treated pulp suspension were vacuum filtered at room temperature through Whatman No. 1 filter paper. Portions of the filtrate (100.0 ml. with or 450.0 ml. without NaOH pulp treatment) were titrated electrometrically to pH 2 with 0.1000N HCl (Harleco concentrate). A Beckman Model N pH meter equipped with a Corning Triple Purpose glass electrode (Cat. No. 476022) was used for this determination.

Two major inflection points were observed in plots of pH vs. volume HCl added. The first, near pH 8, was presumed to be due to free NaOH and the second, near pH 3.0 to 3.5, combined NaOH neutralized by wood acids present in the used or produced by the treatment. The difference in this volume of hydrochloric acid consumed at the two inflection points is used as a measure of the combined sodium hydroxide.

Residual Hydrogen Peroxide

Portions of the filtrate prepared for the analysis of residual sodium hydroxide (250 ml., or 100 ml. diluted to 250 ml.) were treated with 2 g. KI and 25 ml. 18N H<sub>2</sub>SO<sub>4</sub>. The containers were sealed with glass stoppers dipped in saturated KI solutions and allowed to stand for 10 min. The stoppers and sides of the flask were rinsed with deionized water and the contents titrated with 0.1N sodium thiosulfate. The milliequivalents thiosulfate per 100 ml. filtrate was converted to milligram peroxide and divided by the total solids of the neutralized pulp suspension to obtain an estimate of unreacted peroxide in mg. peroxide per 100 g. solids. Knowing the amounts of peroxide, sodium hydroxide and oven-dry groundwood originally present, the residual peroxide was then expressed as a percentage of the amount added.

### Pulp Yield

After the treated pulp suspension had been cooled to room temperature and neutralized to pH 5 with dilute hydrochloric acid; duplicate samples (50-60 g.) were removed, weighed, and evaporated to dryness in 4 to 6 hours at 105° in a forced draft oven. The weight of the oven-dry residue was then used to calculate the total solids of the pulp slurry. A second set of duplicate samples was removed, weighed, and filtered. The filtrate was evaporated to dryness, after being combined with several portions of deionized water used to wash the fiber. The oven-dry filtrate residue divided by the original slurry sample weight gives the soluble solids in the pulp suspension. These data, along with the amount of sodium hydroxide added to the raw pulp, are then used to calculate the yield of treated pulp from this equation:

$$Y \% = 100 \left( \frac{a-b}{a} \right) (1 + 1.46125f)$$

where a = total solids

b = soluble solids

f = g. NaOH added per gram raw pulp

The factor,  $(1 + 1.46125f)$ , is: 1.000, 1.0731, 1.1461, and 1.2192 for 0, 5, 10, and 15 g. NaOH/100 g. pulp, respectively.

### Derivation of the Formula for Pulp Yield

This derivation is based upon the conditions of the ratio of sodium hydroxide to untreated pulp being known and that the oven-dry residue of the treated pulp slurry and of the filtrate can be determined with reasonable accuracy. The assumptions entering the derivation are that no volatile products are produced (that is, the sum of the weights of treated fiber and extracted material equal the

weight of the raw fiber), that the precision required of the calculations is consistent with assuming all of the NaOH is converted to NaCl upon neutralization with HCl (i.e., wood acids are ignored), and that the presence of hydrogen peroxide in some of the treatments has no significant effect upon the determinations of slurry and filtrate solids.

For 100 g. of neutralized slurry of treated pulp, let:

$\underline{H}$  = g. NaOH added

$\underline{N}$  = g. NaCl produced by neutralization

$\underline{F}$  = g. Fibrous treated pulp

$\underline{E}$  = g. Solubilized pulp

$\underline{W}$  = g. water

Assume:

g. Raw pulp =  $\underline{F} + \underline{E}$

$$\underline{N} = \left( \frac{\text{MW NaCl}}{\text{MW NaOH}} \right) \underline{H} = 1.46125 \underline{H} = \underline{kH}$$

$$\text{Yield} = \frac{\underline{F}}{\underline{F} + \underline{E}} = \underline{Y}$$

$$\underline{Y} \% = 100 \left( \frac{\underline{F}}{\underline{F} + \underline{E}} \right)$$

Given:

$$\underline{f} = \frac{\underline{H}}{\underline{F} + \underline{E}} = \frac{\text{g. NaOH added}}{\text{g. raw pulp}}$$

$$\text{then: } \frac{\underline{N}}{\underline{F} + \underline{E}} = \underline{k} \left( \frac{\underline{H}}{\underline{F} + \underline{E}} \right) = \underline{kf}$$

$$\text{thus: } \underline{N} = \underline{kf} (\underline{F} + \underline{E})$$

Determine:

$$\text{Total Slurry Solids} = \frac{\underline{F} + \underline{E} + \underline{N}}{\underline{F} + \underline{E} + \underline{N} + \underline{W}} = \underline{a}$$

$$\text{Filtrate Solids} = \frac{\underline{E} + \underline{N}}{\underline{F} + \underline{E} + \underline{N} + \underline{W}} = \underline{b}$$

then:

$$\underline{a-b} = \frac{\underline{F}}{\underline{F} + \underline{E} + \underline{N} + \underline{W}}$$

$$\underline{F} = (\underline{a-b}) (\underline{F} + \underline{E} + \underline{N} + \underline{W}).$$

$$\text{Since } \underline{N} = \underline{k_f} (\underline{F} + \underline{E})$$

$$\underline{a} = \frac{\underline{F} + \underline{E} + \underline{k_f} (\underline{F} + \underline{E})}{\underline{F} + \underline{E} + \underline{N} + \underline{W}} = \frac{(1 + \underline{k_f}) (\underline{F} + \underline{E})}{(\underline{F} + \underline{E} + \underline{N} + \underline{W})}$$

thus:

$$(\underline{F} + \underline{E}) = \frac{\underline{a} (\underline{F} + \underline{E} + \underline{N} + \underline{W})}{(1 + \underline{k_f})}$$

Therefore

$$\underline{F} = \frac{\underline{F}}{\underline{F} + \underline{E}} \cdot \frac{\underline{a-b}}{\underline{a-b} - \underline{k_f}} \cdot \frac{\underline{F} + \underline{E} + \underline{N} + \underline{W}}{\underline{F} + \underline{E} + \underline{N} + \underline{W}} = \frac{\underline{a-b}}{\underline{a-b} - \underline{k_f}} \cdot \frac{\underline{F}}{\underline{F} + \underline{E}}$$

$$\underline{F} = \frac{\underline{a-b}}{\underline{a-b} - \underline{k_f}} \cdot \underline{F}$$

$$\underline{F} = \frac{\underline{a-b}}{\underline{a-b} - \underline{k_f}} \cdot \underline{F}$$

$$\underline{F} = \frac{\underline{a-b}}{\underline{a-b} - \underline{k_f}} \cdot \underline{F}$$